Synthesis and Investigations Into the Reactivity of Electron Deficient Organoscandium Complexes

Thesis by

Mark Edward Thompson

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to the best chemist I've ever known,

Donald A. Thompson

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ABSTRACT

A new class of coordinatively unsaturated, monomeric scandium complexes, Cp^*_2ScR ($Cp^* = \eta^5$-$C_5(CH_3)_5$; R = H, alkyl, aryl, halide) have been prepared. Cp^*_2ScCl is prepared by the reaction of $ScCl_3(THF)_3$ with $LiCp^*$, and Cp^*_2ScR (R = CH_3, C_6H_5, $C_6H_4CH_3$, $CH_2C_6H_5$) by the reaction of Cp^*_2ScCl with the appropriate organoalkali reagent. Cp^*_2ScR complexes react readily with H_2 to give RH and Cp^*_2ScH. The hydride ligand exchanges rapidly with hydrogen gas and inserts olefins to give alkyl complexes (e.g. $Cp^*_2ScCH_2CH_3$). Cp^*_2ScH reacts with allene to give $Cp^*_2Sc(\eta^3$-$CH_2CH{=}CH_2)$. Cp^*_2ScR and Cp^*_2ScH react with pyridine to give $Cp^*_2Sc(C,N$-η^2-$C_5H_4N)$. The crystal structure of this complex was determined and is reported herein.

Spectroscopic data for $Cp^*_2ScCH_3$ and $Cp^*_2ScCH_2CH_3$ and crystalographic data for the former indicate that the methyl ligand is bound to scandium in a conventional manner, while the ethyl ligand may participate in an agostic interaction.

The reactions of scandium alkyl, aryl and hydride complexes were investigated. H/D exchange between H_2, arenes and the 1^o and 2^o C-H bonds of alkanes is catalyzed by Cp^*_2ScH. In C_6H_6 solution Cp^*_2ScH and $Cp^*_2ScC_6H_5$ are in equilibrium, ΔH^o = 6.7 $\pm$ 0.3 kcal/mole and ΔS^o = 1.5 $\pm$ 0.1 e.u.. Thus in this system a scandium-hydride bond is 1.5 $\pm$ 0.4 kcal/mole stronger than a scandium-phenyl bond. $Cp^*_2ScCH_3$ reacts with a wide range of hydrocarbons (RH) by C-H bond activation to give CH_4 and Cp^*_2ScR (RH = $^{13}CH_4$,

arenes, styrenes, propyne). From the reactions of $Cp^*_2ScCH_3$ with styrenes, the activation parameters ($\Delta H^{\ddagger}$ = 11.5-12.6 kcal/mole, $\Delta S^{\ddagger}$ = -34 to -38 e.u.) for these C-H activation reactions were determined. A deuterium isotope effect of 2.9 is observed for the intermolecular activation of C-H in the reaction of $Cp^*_2ScCH_3$ with benzene. Very small differences in the rates of vinylic C-H bond activation for $CH_2=CHC_6H_4X$-para (X = CF_3, OCH_3), and the aryl C-H bonds of C_6H_5X (X = CF_3, H, CH_3, $N(CH_3)_2$), as well as the positional nonselectivity for the activation of the meta and para C-H bonds of toluene indicate that the scandium center does not interact substantially with the π-system of these substrates in the transition states for these reactions. Thus for these sterically encumbered organoscandium compounds, sp^2 C-H bond activation occurs without formation of a π-complex. A general mechanism for these C-H and H-H activation reactions is proposed, and is termed "σ-bond metathesis".

The reactions of Cp^*_2ScR complexes (R = hydride, alkyl, aryl) with small olefins and alkynes were examined. The hydride, methyl and benzyl complexes function as ethylene polymerization catalysts, while $Cp^*_2ScC_6H_5$ does not react. Cp^*_2ScH and $Cp^*_2ScCH_3$ react stoichiometrically with propene by a series of insertion and vinylic C-H activation reaction. The final scandium product in both cases is trans-$Cp^*_2ScCH=CHCH_3$. The scandium allyl complex, $Cp^*_2Sc(\eta^3-CH_2CH=CH_2)$, is not observed and is not a reaction intermediate.

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ABBREVIATIONS

atm	atmospheres
br	broad
Cp	cyclopentadienyl, η^5-C_5H_5
Cp*	pentamethylcyclopentadienyl, η^5-$C_5(CH_3)_5$
d	doublet
i	iso
m	multiplet (NMR), medium (IR)
m	meta
n	normal
o	ortho
p	para
q	quartet
sh	shoulder
s	singlet (NMR), strong (IR)
t	trans
w	weak

Synthesis and Structure of Alkyl and Hydride Derivatives of Permethylscandocene

INTRODUCTION

Over the past three decades the organometallic chemistry of scandium has been largely ignored. Scandium has been traditionally grouped with the lanthanides, based on its low electronegativity and lack of accessible oxidation states other than trivalent. However, scandium's ionic radius (0.81 Å for Sc (III)) [1] is considerably smaller than those seen for the lanthanides (ranging from 1.1 Å for Ce (III) to 0.93 Å for Lu (III)),[1] and is comparable to some transition metals in their common oxidation states (Zr (IV) = 0.80 Å, V(III) = 0.78 Å).[1] The low electronegativity and ionic radius of scandium suggests that its organometallic complexes may exhibit unique reactivity patterns.

ScR_3 complexes are commonly polymeric (<u>i.e.</u> $[ScCp_3]_x$,[2] $[Sc(C_6H_5)_3]_x$ [3] and $[Sc(C{\equiv}CC_6H_5)_3]_x$) [3], and are insoluble in nonreactive solvents. Biscyclopentadienylscandium-based compounds, however, are isolated as stable monomeric and dimeric species. $[Cp_2ScCl]_2$ and $[Cp_2ScC{\equiv}CC_6H_5]_2$ [4] are both dimeric with bridging chloride and phenylethynyl ligands, respectively, while $Cp_2Sc(THF)CH_3$ [5] and $Cp_2Sc(\eta^3\text{-allyl})$ [4] are monomeric. Complexes containing bridging main group atoms have also been reported, as in $Cp_2Sc(\mu\text{-}CH_3)_2Al(CH_3)_2$ [6] and $Cp_2Sc(\mu\text{-}CH_2)P(CH_3)_2$ [7]. Although C_5H_5 is sterically demanding enough to prevent oligo-

merization in Cp_2Sc-based complexes, it is not sufficiently bulky to prevent coordination of a datively bound ligand, which gives all reported scandocene-based complexes an electron count of 16.

Previous work in our group has shown that monomeric, coordinatively unsaturated hydride and alkyl complexes of group IV metals, i.e. $Cp^*_2MR_2$ (M = Ti, Zr, Hf; R = alkyl, hydride; $Cp^* = \eta^5\text{-}C_5Me_5$) exhibit high reactivity toward CO, H_2, olefins and C-H bonds.[8] This is attributed to the high Lewis acidity of the metal center and the coordinative unsaturation of these 16 electron, d^0 complexes. We expect that analogous scandium complexes should be even more reactive than their group IV counterparts, because scandium is a stronger Lewis acid than the group IV elements, and Cp^*_2ScR would be a 14 electron, d^0 complex with two vacant orbitals.[9]

Herein, we report the synthesis of a new class of coordinatively unsaturated, monomeric scandium complexes, Cp^*_2ScR (R = Cl, alkyl, aryl, hydride). The alkyl, aryl and hydride complexes react readily with H_2 at -80^oC, and activation C-H bonds by these complexes is observed at room temperature. These complexes act as ethylene polymerization catalysts, and react stoichiometrically with propene and other olefins. In this chapter the synthesis of these complexes and their reactivity toward H_2 and pyridine (leading

to $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$) are discussed. The bonding of the methyl and ethyl ligands of $Cp^*_2ScCH_3$ and $Cp^*_2ScCH_2CH_3$ are also discussed. The general discussions of C-H activation and olefin reactions by these complexes are covered in chapters 2 and 3, respectively.

RESULTS and DISCUSSION

Synthesis of Alkyl and Hydride Complexes of Permethylscandocene. We felt that a logical first step into decamethylscandocene complexes was the synthesis of a halide compound. $Cp^*_2Sc(THF)Cl$ is the product formed initially in the reaction of LiCp* with $ScCl_3(THF)_3$, (eq 1).

$$ScCl_3(THF)_3 + 2LiCp^* \longrightarrow Cp^*_2Sc(THF)Cl + 2LiCl + 2THF \quad (1)$$

The THF molecule of $Cp^*_2Sc(THF)Cl$ is easily removed by heating in vacuo, to give Cp^*_2ScCl, (eq 2).

$$Cp^*_2Sc(THF)Cl \xrightarrow[10^{-4}\ torr]{120^oC} Cp^*_2ScCl + THF \quad (2)$$

The product, Cp^*_2ScCl, is generally obtained by sublimation (120°C, 10^{-4} torr) directly from the residue of the initial reaction mixture after the solvent has been removed in vacuo. A solution molecular weight measurement (in C_6H_6) and mass spectral analysis show that Cp^*_2ScCl is monomeric in solution and in the gas phase. In contrast, Cp_2ScCl is a dimer with bridging chloride ligands.[4] Moreover, $Cp_2Sc(THF)Cl$ does not dissociate THF on sublimation.[10]

Decamethylscandocene chloride readily undergoes metathesis reactions. $Cp^*_2ScC_6H_4CH_3$ (ortho, meta or para)

can be prepared in pure hydrocarbon solvent, by the reaction of Cp^*_2ScCl with the appropriate tolyllithium reagent, (eq 3).

$$Cp^*_2ScCl + LiC_6H_4CH_3 \xrightarrow[\text{toluene}]{} Cp^*_2ScC_6H_4CH_3 + LiCl \quad (3)$$

$Cp^*_2ScCH_3$ and $Cp^*_2ScC_6H_5$ are made by treating Cp^*_2ScCl with a diethylether solution of the corresponding lithium reagent, (eqs 4 and 5).

$$Cp^*_2ScCl + LiCH_3 \xrightarrow[\text{toluene}]{Et_2O} Cp^*_2ScCH_3 + LiCl \quad (4)$$

$$Cp^*_2ScCl + LiC_6H_5 \xrightarrow[\text{toluene}]{Et_2O} Cp^*_2ScC_6H_5 + LiCl \quad (5)$$

If these reactions are carried out in the presence of THF, the scandium alkyl or aryl complex is not formed, but rather $Cp^*_2Sc(THF)Cl$ is isolated, which is unreactive towards LiMe and LiC_6H_5. One complex, $Cp^*_2ScCH_2C_6H_5$, can be synthesized in the presence of THF, if $KCH_2C_6H_5$ is used, (eq 6).

$$Cp^*_2ScCl + KCH_2C_6H_5 \xrightarrow[\text{toluene}]{THF} Cp^*_2ScCH_2C_6H_5 + KCl \quad (6)$$

Presumably, $KCH_2C_6H_5$ is potent enough to react with $Cp^*_2Sc(THF)Cl$.

Permethylscandocene complexes have a very crowded coordination sphere, which can be seen in their base coordi-

nating abilities. Both C_6H_5 and $CH_2C_6H_5$ ligands are too bulky to allow coordination of THF, while Cp^*_2ScMe will coordinate a THF molecule to give $Cp^*_2Sc(THF)Me$. This THF ligand is bound tightly enough to allow crystallization of an analytically pure sample of $Cp^*_2Sc(THF)Me$ in the absence of excess THF. The π cloud of the phenyl portion of a benzyl ligand can act as an electron donor ligand, making the benzyl η^3 coordinate. However, the NMR spectrum of the phenyl portion of the benzyl ligand of $Cp^*_2ScCH_2C_6H_5$ remains a simple ABC pattern on cooling to -90^oC. We feel that this is an indication of η^1 coordination of the the benzyl ligand, but an η^3 (allyl like) structure which is rapidly exchanging sides of the phenyl ring, even at -90^oC, can not be ruled out. Solution molecular weight determinations show that Cp^*_2ScR (R = CH_3, $CH_2C_6H_5$) complexes are monomeric. Moreover, a crystal structure determination shows that $Cp^*_2ScCH_3$ is also monomeric in the solid state (vide infra). All of these scandium alkyl and aryl complexes are formally 14 electron species, with two vacant orbitals.[9]

Cp^*_2ScR (R = CH_3, C_6H_5, $CH_2C_6H_5$, $C_6H_4CH_3$) reacts cleanly with hydrogen to give RH and a single scandium species, which we presume is $[Cp^*_2ScH]_x$, (eq 7).

$$Cp^*_2ScR + H_2 \xrightarrow[\text{hexane}]{} 1/x[Cp^*_2ScH]_x + RH \qquad (7)$$

This scandium hydride complex is unstable under less than one atmosphere of hydrogen. However, if a hexane solution of Cp^*_2ScH (under excess H_2) is cooled to -78°C, a solid precipitates, which can be isolated. Unfortunately, this solid decomposes immediately on addition of solvent, preventing the measurement of its molecular weight. If four atmospheres of hydrogen are put over a benzene solution of Cp^*_2ScH, it can be heated to 150°C for over a week with no sign of decomposition of the scandium complex (monitored by ^1H NMR). When R in (eq 7) is $CH_2C_6H_5$, the reaction consumes 0.93 equiv. of hydrogen and yields 1.0 equiv. of $C_6H_5CH_3$. The kinetics of the reaction of Cp^*_2ScR (R = alkyl, aryl) with H_2 were not examined in detail; however, a half-life of 4-5 minutes was observed for the reaction of $Cp^*_2ScCH_3$ with H_2 (2 atm) at -78°C.

A common way to demonstrate the existence of early transition metal hydrides is by their reaction with CH_3I to give CH_4. When Cp^*_2ScH, generated in situ, is treated with CH_3I, CH_4 is formed, (eq 8).

$$Cp^*_2ScH + CH_3I \longrightarrow Cp^*_2ScI + CH_4 \qquad (8)$$

Solutions of Cp^*_2ScH catalyze H-D exchange between H_2 and D_2, giving statistical mixtures of H_2, HD and D_2, (eq 9).

$$H_2 + D_2 \xrightarrow[[Cp^*_2ScH]]{} H_2 + 2HD + D_2 \qquad (9)$$

This exchange reaction is common for coordinatively unsaturated transition metal hydride complexes,[11] and isoelectronic main group metal hydrides.[12]

The room temperature NMR spectrum of a methylcyclohexane solution Cp^*_2ScH under four atmospheres of hydrogen shows only a single resonance for the Cp* protons and no resonances assignable to the hydride ligand or H_2. Failure to observe these signals could be due to broadening of the hydride resonance by the strong quadrupolar moment of the scandium nucleus (-0.22 barns, 100% spin 7/2),[13] or rapid exchange of the hydride with hydrogen gas, or both. Quadrupolar broadening can often be decreased by changing the temperature; this changes the quadrupolar relaxation time, giving rise to sharper lines for the observed nucleus.[14] To determine the importance of quadrupolar broadening in this compound, the NMR sample was heated to 120°C. At this temperature a new, broad peak appeared at 6.1 ppm (full width at half height (fwhh) = 26 Hz.), which must be an average resonance for the scandium hydride and the protons of H_2, since a signal for hydrogen (δ = 4.5 ppm in C_7D_{14}) is not observed. This averaging process is facile even at lower temperatures. When this NMR sample was cooled to -80°C, a new, broad resonance again appeared, this time at 6.2 ppm (fwhh = 32 Hz.); a similar resonance is observed in toluene at 6.65 ppm(fwhh = 33 Hz.). This exchange process could not be frozen out in either methylcyclohexane or

toluene; if the sample is cooled to -95°C, a single resonance is still observed for the hydride and hydrogen. The NMR spectrum of Cp^*_2ScH in the absence of H_2 has not been measured, but if the observed resonance is a simple weighted average, the chemical shift of the hydride ligand can be calculated from the observed chemical shift and the concentrations of H_2 and Cp^*_2ScH.[15] We calculate a chemical shift of 7.3(3) ppm for this hydride in toluene-d_8.

If the scandium alkyl hydrogenation reaction is carried out in the presence of THF, an isolable hydride complex is formed, (eq 10).

$$Cp^*_2ScR + H_2 \xrightarrow{THF} Cp^*_2Sc(THF)H + CH_4 \qquad (10)$$

$$R = CH_3,\ C_6H_5,\ CH_2C_6H_5,\ C_6H_4CH_3$$

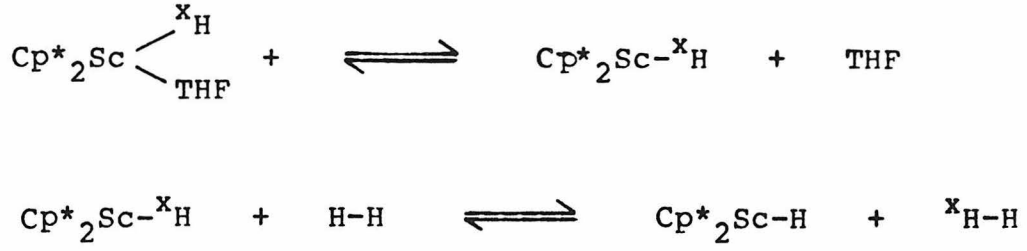
$Cp^*_2Sc(THF)H$ decomposes over a period of days at room temperature, but is stable for months at -10°C. $Cp^*_2Sc(THF)D$ shows the expected shift in the ν(Sc-H) IR band from 1390 cm^{-1} to 990 cm^{-1}. Like Cp^*_2ScH, $Cp^*_2Sc(THF)H$ reacts with CH_3I to give CH_4, (eq 11).

$$Cp^*_2Sc(THF)H + CH_3I \longrightarrow Cp^*_2Sc(THF)I + CH_4 \qquad (11)$$

Solution molecular weight studies show that $Cp^*_2Sc(THF)H$ is monomeric.

The room temperature NMR spectrum of $Cp^*_2Sc(THF)H$ shows peaks assignable to the Cp* ligand and the α and β positions

of the THF ligand, but no resonance is observed for the scandium hydride. On cooling the sample to -60°C, a new peak grows out of the baseline at 4.8 ppm, and sharpens on further cooling (fwhh (-90°C) = 18 Hz.). If four atmospheres of hydrogen is put over the solution, the resonance at 4.8 ppm remains unchanged and a sharp resonance for H_2 (4.5 ppm) is observed. We therefore assign the peak at 4.8 ppm to the scandium hydride. Unlike Cp^*_2ScH, the hydride of $Cp^*_2Sc(THF)H$ is not exchanging with H_2 rapidly at low temperatures; this exchange process is not evident on the NMR time scale (90 MHz) until -20°C and warmer. Even though the hydride resonance disappears above -60°C, due to quadrupolar broadening,the signal for H_2 remains until -20°C. In the presence of 10 equiv. of THF this signal persists until 0°C. The fact that this hydride-hydrogen exchange occurs at low temperatures for Cp^*_2ScH, and at a much higher temperature for $Cp^*_2Sc(THF)H$, suggests that the species actually engaged in this exchange process is Cp^*_2ScH, and that $Cp^*_2Sc(THF)H$ must dissociate the THF ligand for its hydride to exchange with H_2, as shown in Scheme 1. In support of this proposal, excess THF inhibits this exchange further , since the added THF should shift the equilibrium toward $Cp^*_2Sc(THF)H$.



Scheme 1

Although Cp^*_2ScH could not be isolated pure, it has proved to be a valuable reagent when generated in situ. We have found a good route into alkyl and allyl complexes to be the insertion of olefins into this scandium hydride bond, (eqs 12, 13 and 14).

$$Cp^*_2ScH + H_2C{=}CH_2 \longrightarrow Cp^*_2ScCH_2CH_3 \quad (12)$$

$$Cp^*_2ScH + H_2C{=}CHCH_3 \longrightarrow Cp^*_2ScCH_2CH_2CH_3 \quad (13)$$

$$Cp^*_2ScH + H_2C{=}CH{=}CH_2 \longrightarrow Cp^*_2Sc(\eta^3\text{-}CH_2CH{=}CH_2) \quad (14)$$

These insertion reactions were conducted at -78^oC; at this temperature Cp^*_2ScH reacts with only a single equivalent of olefin to give the observed products. These complexes are all stable to olefin loss at room temperature.

NMR coalescence of the syn and anti proton signals of the allylic CH_2 groups, of $Cp^*_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$, is observed near room temperature. At low temperature (-50^oC) a static η^3-structure is observed for the allyl ligand. The signals for the anti and syn protons are doublets at 3.93 ppm and

2.07 ppm, respectively, coupled to the central allylic proton by 15.6 Hz and 9.7 Hz, respectively; no geminal coupling is observed. The central proton is a non-first order multiplet. If the sample is heated to 90°C the syn and anti protons become equivalent,[16] giving rise to a doublet at 2.86 ppm, which is coupled to the central proton by 12.7 Hz. The central proton is obscured by solvent resonances in toluene but is a first order quintet at 6.95 ppm in C_6D_{12} ($^3J_{H-H}$ = 12.7 Hz).

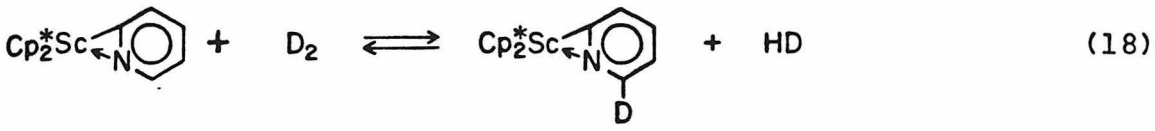
Cp^*_2ScR (R = CH_3, C_6H_5, $CH_2C_6H_5$, $C_6H_4CH_3$), as well as Cp^*_2ScH and $Cp^*_2Sc(THF)H$, react cleanly with pyridine to give an η^2-orthometallated pyridyl complex, (eqs 15, 16 and 17).

$$Cp^*_2ScR + C_5H_5N \longrightarrow Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N) + RH \qquad (15)$$

$$Cp^*_2ScH + C_5H_5N \longrightarrow Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N) + H_2 \qquad (16)$$

$$Cp^*_2Sc(THF)H + C_5H_5N \longrightarrow Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N) + THF + H_2 \qquad (17)$$

The reaction of Cp^*_2ScH with pyridine presumably goes through a $Cp^*_2Sc(py)H$ intermediate, analogous to $Cp^*_2Sc(THF)H$. Moreover, in the reaction of $Cp^*_2ScCH_3$, the intermediate, $Cp^*_2Sc(py)CH_3$, can be observed before it reacts to give $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$ and CH_4. The reversibility of the reaction of Cp^*_2ScH with pyridine is seen in the reaction of D_2 with $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$, (eq 18).



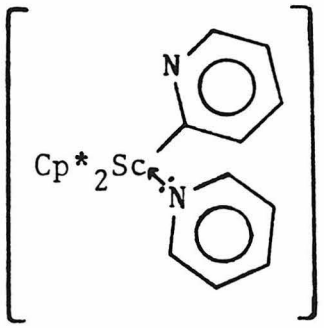
(18)

Deuterium incorporation takes place in only the ortho positions of the pyridyl ligand.

In the reaction of $Cp^*_2Sc(THF)H$ with pyridine, an 18 electron intermediate, $Cp^*_2Sc(THF)(py)H$, is possible. There is no direct evidence against such an intermediate, however, the steric crowding in it would be great. A similar intermediate is possible in the reaction of $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$ with pyridine-$\underline{d}_5$, (eq 19).

$$Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N) + C_5D_5N \text{ -----> } Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5D_4N) + C_5H_4DN \quad (18)$$

Again, steric crowding would be large if the pyridyl ligand remained η^2 when the added pyridine coordinated. A 16 electron structure like (A) is much more favored sterically.

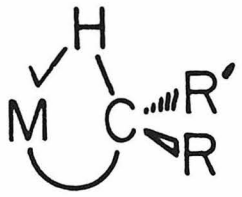


(A)

An x-ray structural determination was performed on $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$, the ORTEP drawing and skeletal view of

which are shown in Figures 1 and 2, respectively. The pyridyl ligand is disordered; the carbon and nitrogen atoms bound to scandium are indistinguishable. The two atoms were modeled as 50% carbon and 50% nitrogen.

Structure and Bonding of $Cp^*_2ScCH_3$ and $Cp^*_2ScCH_2CH_3$. Cp^*_2ScR (R = alkyl) complexes are very electron deficient. They are formally 14 electron species with two vacant orbitals. At least one of these orbitals is accessible for bonding, which can be seen in the formation of $Cp^*_2Sc(THF)CH_3$ and $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$. We felt that these 14 electron alkyl complexes would be excellent candidates for a three-center two-electron bond with one of the C-H bonds of the alkyl ligand, as in (B).



(B)

Examples of this type of interaction (termed agostic) have been reviewed by Brookhart and Green.[17] By participating in an agostic interaction, the metal center increases its electron count by two; this would make a scandium alkyl complex a 16 electron one. Agostic interactions are only seen in electron deficient complexes and are most common in

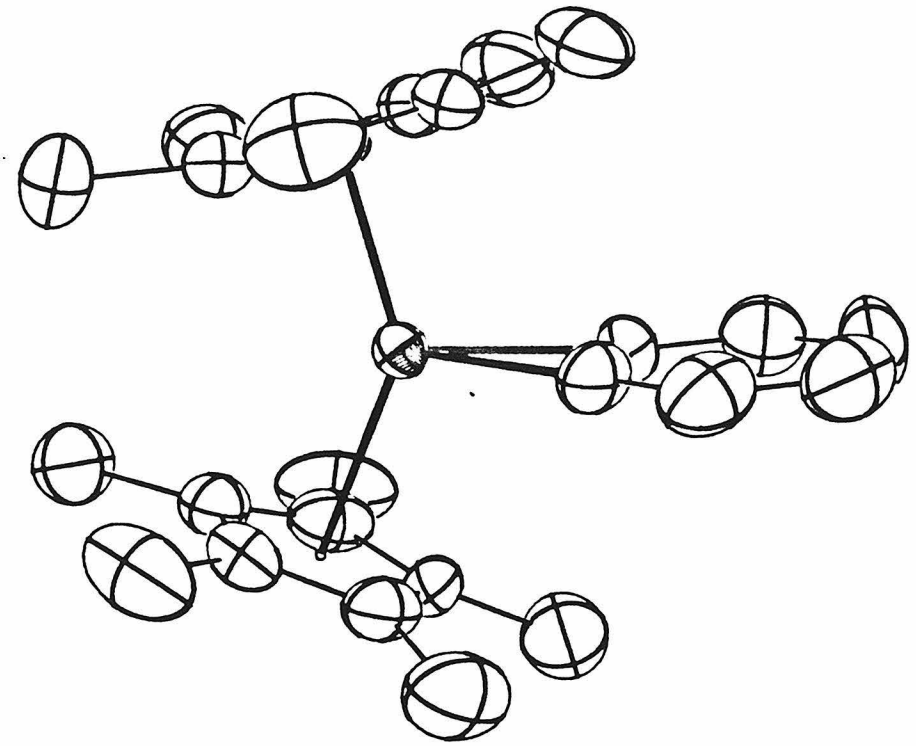


Figure 1. ORTEP drawing of $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$.

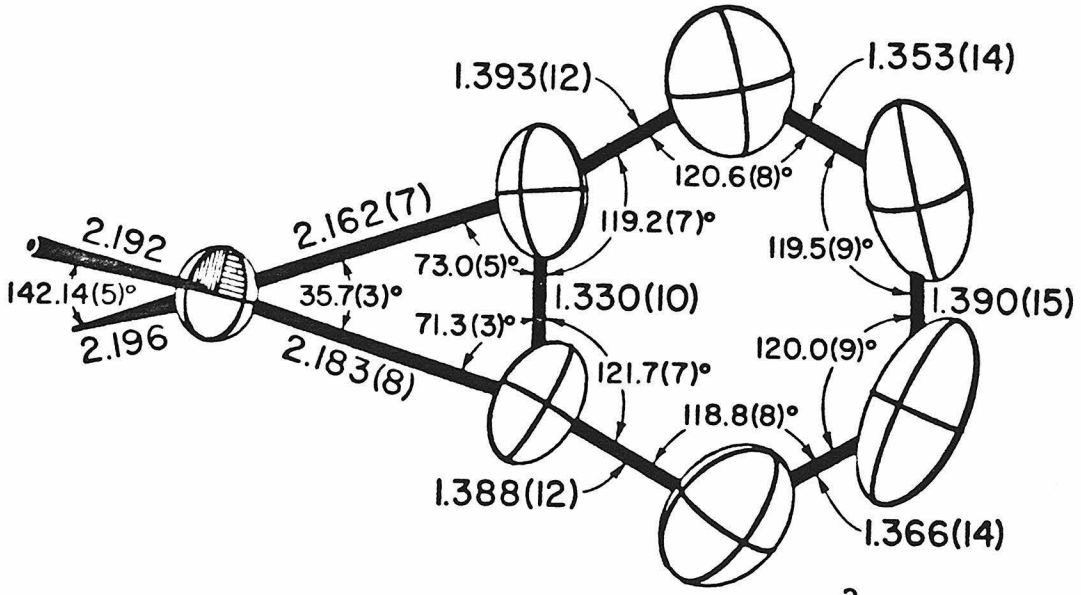


Figure 2. Skeletal view of $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$ with bond distances (Å) and angles (°).

highly deficient ones, such as $(Me_2PCH_2CH_2PMe_2)TiCl_3R$ ($R = CH_3$, CH_2CH_3).[18] The titanium ethyl complex has an agostic interaction with a β C-H bond.

The proton NMR spectrum of $Cp^*_2ScCH_3$ shows a methyl resonance that remains a singlet on cooling to -90°C; $Cp^*_2Sc^{13}CH_3$ shows a doublet with $^1J_{C-H}$ = 111 Hz. The sixteen electron scandium methyl complex, $Cp^*_2Sc(THF)^{13}CH_3$, also gives a doublet with $^1J_{C-H}$ = 111 Hz for the methyl resonance. The spectrum of the ethyl ligand of $Cp^*_2ScCH_2CH_3$ is a simple first order pattern with a $^3J_{H-H}$ = 5.6 Hz, which does not change on cooling to -80°C; $^1J_{C-H}$ for the α and β carbons are 128 and 120 Hz, respectively. Agostic interactions are often fluxional, such that NMR spectra of agostic ligands show an averaged resonance for the bridging (agostic) and terminal (non-agostic) protons, rather than discrete resonances for each type of proton. Partial deuteration of an agostic ligand can provide evidence for a fluxional agostic interaction. A large chemical shift and $^1J_{C-H}$ difference is generally observed between a partially deuterated agostic ligand and a perprotonic one. This difference is attributed to an increase in metal hydride character for the protons of the partially deuterated ligand relative to those of the perprotonic one, which shifts the proton resonance and lowers the C-H coupling constant for the partially deuterated ligand relative to the perprotonic one.[17] These chemical shift differences are typically

0.35 ppm or greater for agostic methyl ligands. The chemical shift difference between $Cp^*_2ScCH_3$ (δ_{CH_3} = 0.07 ppm) and $Cp^*_2ScCH_2D$, as well as for several other methyl compounds, are given in Table 1.

TABLE 1: Chemical shift differences between CH_3 and CH_2D ligands.

compound	$\Delta\delta$ ($\delta_{CH_3} - \delta_{CH_2D}$) (ppm)
$Cp^*_2ScCH_3$	0.057
$Cp^*_2Sc(THF)CH_3$	0.047
$Cp_2W(CH_3)_2$[a]	0.020
CH_4[a]	0.019

[a]Non-agostic compound.

The chemical shift difference for $Cp^*_2ScCH_3$ vs. $Cp^*_2ScCH_2D$ is rather small. A partially deuterated ethyl complex, $Cp^*_2Sc^{13}CH_2{}^{13}CH_2D$, was synthesized, and its NMR spectrum compared to that of $Cp^*_2Sc^{13}CH_2{}^{13}CH_3$. The methyl group of the ethyl ligand is shifted from 0.139 ppm to 0.049 ppm ($\Delta\delta$ = 0.090 ppm) on deuteration. The C-H coupling constant for both the CH_3 and the CH_2D group is 120 Hz, while the CH_2 group has a $^1J_{C-H}$ of 129 Hz.

Infrared spectroscopy can also be used to detect an agostic interaction. Agostic alkyl ligands often have low energy C-H stretching bands in the region ν(C-H) = ca. 2700-2400 cm^{-1}.[17] $Cp^*_2ScCH_3$ does not exhibit low energy ν(C-H)

modes. Moreover, $Cp^*_2ScCD_3$ has two ν(C-D) bands at 2195 and 2152 cm^{-1}. By comparison CD_3I has ν(C-D) bands at 2160 and 2140 cm^{-1}. $Cp^*_2ScCH_2CH_3$, however, has prominent low energy ν(C-H) bands at 2593, 2503 and 2440 cm^{-1}. The existence of these bands suggests strongly that and agostic interaction is present in the scandium ethyl complex. The NMR and IR data appear contradictory. One possible explanation for this is that an α-agostic interaction is present in $Cp^*_2ScCH_2CH_3$. We did not partially deuterate the α position, so a large difference between its room and low temperature chemical shifts and coupling constants may not be observed. Another possibility is that a β-agostic interaction is present and both the chemical shift and coupling constant of the methyl group are not altered on partial deuteration in the same manner as other reported agostic ligands. In support of this, a crystal structure determination showed $(Me_2PCH_2CH_2PMe_2)TiCl_3CH_2CH_3$ has a β-agostic interaction with the ethyl ligand,[18] but the NMR spectra of the perprotio and β-monodeutero complexes are identical.[19] It is also possible that an agostic interaction exists in the solid state but not in solution. The best way to ascertain if a complex has an agostic interaction is to determine its crystal structure. A crystal structure of $Cp^*_2ScCH_2CH_3$ is now in progress.

The crystal structure of $Cp^*_2ScCH_3$ is interesting not only as it pertains to the question of agostisism, but also

how it compares to the isoelectronic $[Cp^*_2LuCH_3]_2$ structure. $[Cp^*_2LuCH_3]_2$ is an asymmetric dimer with one bridging and one terminal methyl ligand, where the bridging methyl is in a nearly linear Lu-C-Lu configuration.[20] The ORTEP drawing of $Cp^*_2ScCH_3$ is shown in Figure 3. The x-ray crystal structure confirms that $Cp^*_2ScCH_3$ is monomeric in the solid state. Unfortunately, the data set collected at 25°C showed significant static and dynamic disorder in the molecule; we could not locate the methyl ligand hydrogen atoms, but information about the bonding of the methyl ligand can still be obtained from the structure. The methyl carbon has a spherical thermal ellipsoid which lies only 0.01 A out of the plane formed by the ring centroids and the scandium atom; this is consistent with simple covalent-only bonding. If there were a significant agostic interaction, the methyl carbon should have been moved out of this plane. The methyl ligand of $(Me_2PCH_2CH_2PMe_2)TiCl_3CH_3$ is distorted appreciably from the idealized octahedral site by its agostic interaction. A low temperature data set should remove the disorder, allowing us to locate the hydrogens, and answer the question of agostisism in this scandium methyl complex, but all of the spectroscopic data we have compiled speaks against the existence of an agostic interaction for this compound. Theoretical calculations suggest that for an agostic interaction to be the ground state, a vacant orbital of the proper symmetry and orientation, as well as a weak-

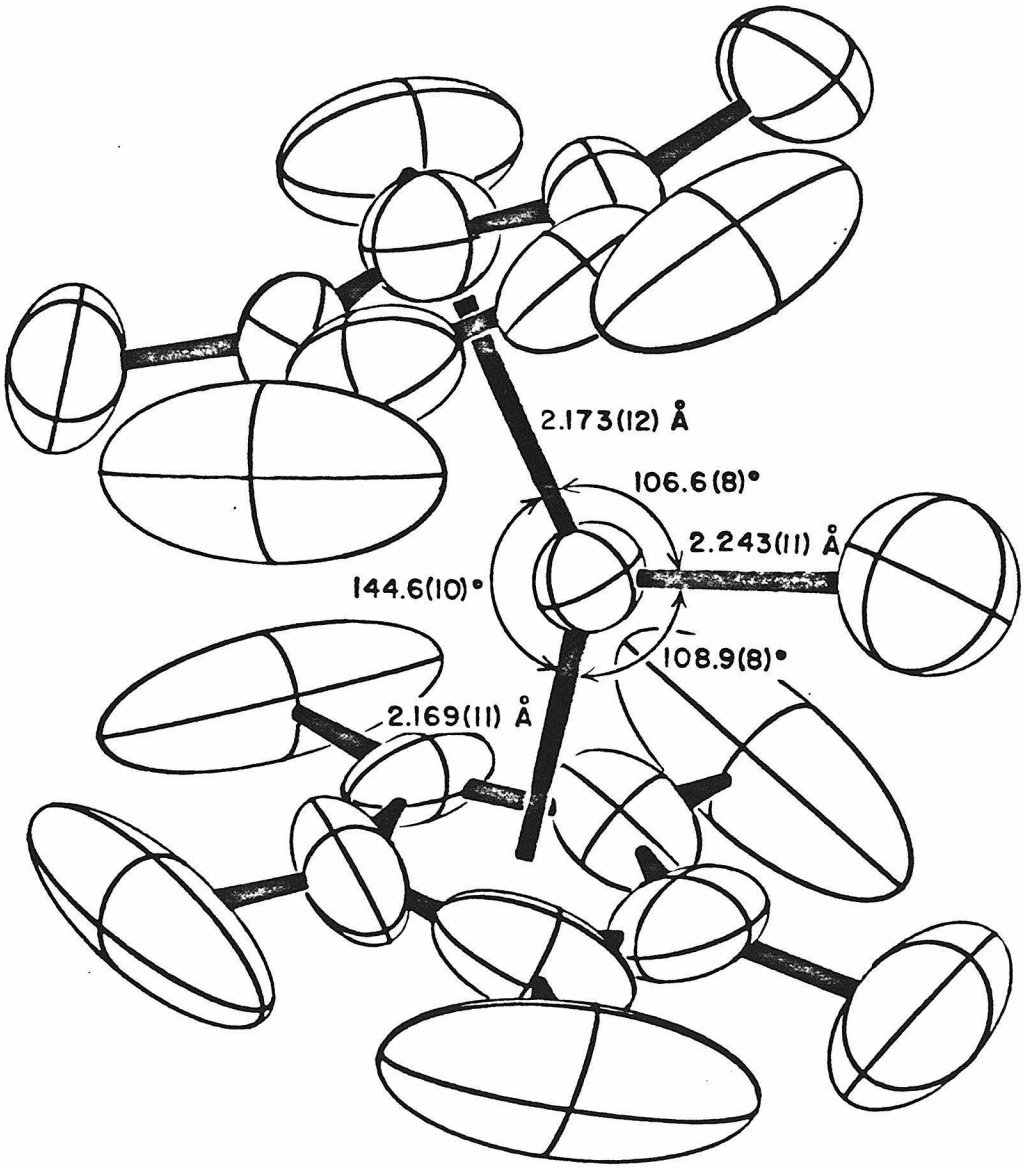


Figure 3. ORTEP drawing of $Cp^*_2ScCH_3$.

ened $M-CH_3$ bond are required.[21] These calculations predict that L_2M-CH_3 complexes should not have an agostic ground state, which is consistent with our observations for $Cp^*_2ScCH_3$.

EXPERIMENTAL

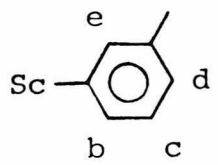
General Considerations. All manipulations were carried out using either high vacuum line or glove box techniques. Gas evolution measurements were performed using standard Toepler techniques, and the gases were identified by either mass spectroscopy or NMR. Xylene was distilled from CaH_2 and degassed. THF was purified by vacuum transfer from sodium benzophenone. All other solvents were purified by vacuum transfer first from $LiAlH_4$, then from titanocene, prepared as described earlier.[22] Sc_2O_3, 99% (Alpha Chem. Co.), CH_2DI, $^{13}CH_3I$ and $^{13}C_2H_4$ (MSD Isotopes) were used directly with no purification. NMR solvents, benzene-$\underline{d}_6$, toluene-$\underline{d}_8$ (Stohler Inc.) and methylcyclohexane-$\underline{d}_{14}$ (MSD Isotopes), were vacuum transferred from activated 4 Å molecular sieves, then from titanocene. Hydrogen was purified by passage over activated 4 Å molecular sieves and MnO on vermiculite.[23] LiCp*,[24] $ScCl_3(THF)_3$,[25] and $Cp_2W(CH_3)_2$ [26] were prepared by previously published procedures.

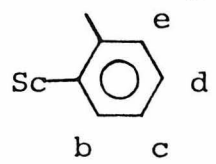
Room temperature ^1H NMR spectra were recorded in C_6D_6 with an internal $Si(CH_3)_4$ reference on a Varian EM-390 (90 MHz) spectrometer. Low and high temperature NMR spectra were recorded on a JOEL FX-90Q spectrometer in either C_7D_8 or C_7D_{14}. All NMR spectra are listed in Table 3. Infrared spectra were run as nujol mulls on KBr plates and recorded on a Beckman IR-4240 spectrometer. Mass spectra were

Table 2. ^{1}H and ^{13}C NMR spectroscopic data.*

Compound	Assignment	δ (ppm)	Coupling	Comments
Cp^*_2ScCl	$C_5(CH_3)_5$	1.83 s		
$Cp^*_2ScCH_3$	a	1.87 s		
a b	b	0.07 s		
$Cp^*_2ScCH_2D$	a	1.87 s		
a b	b	0.013 t	$^{2}J = 1.8$	
$Cp^*_2Sc^{13}CH_3$	a	1.87 s		
a b	b	0.07 d	$^{1}J = 111$	
$Cp^*_2Sc(THF)CH_3$	a	1.91 s		
	b (α)	3.40 m		
a b c	b (β)	1.31 m		
	c	-0.19 s		

Compound	Assignment	δ (ppm)	Coupling	Comments
$Cp^*_2ScCH_2C_6H_5$	a	1.77 s		
a b c	b	2.23 s		
	c	6.8-7.1 m		
	ortho	6.78 d	8.0	500 MHz
	c meta	6.95 t	7.5	
	para	7.15 t	8.5	
$Cp^*_2ScC_6H_5$	a	1.73 s		
a b	b	7.0-7.4 m		
$Cp^*_2Sc\text{-}C_6H_4\text{-}CH_3\text{-}p$	a	1.76 s		500 MHz
a b c	b	6.92 d	5.4	
	b	7.26 d	5.4	
	c	2.33 s		
$Cp^*_2Sc\text{-}C_6H_4\text{-}CH_3\text{-}m$	a	1.77 s		500 Mhz
a f	b	6.85 d	5.7	
	c	7.32 t	5.7	
	d	7.07 d	5.7	
	e	6.78 s		
	f	2.43 s		



Compound	Assignment	δ (ppm)	Coupling	Comments
$Cp^*_2Sc\text{-}C_6H_4CH_3\text{-}o$ 	a	1.77 s		500 MHz
	b	6.32 d	5.3	
	c + d	7.20 m		
	e	7.26 d	6.0	
	f	2.12 s		
Cp^*_2ScH a b	a	1.90 s		-80^oC, C_7D_8
	b	7.3 (calculated)		
$Cp^*_2Sc(THF)H$ a b c	a	2.08 s		
	b (α)	3.43 m		
	b (β)	1.25 m		
	c	4.80 s		
$Cp^*_2ScCH_2CH_3$ a b c	a	1.88 s		
	b	0.97 q	6.8	
	c	0.18 t	6.8	
$Cp^*_2Sc^{13}CH_2{}^{13}CH_3$ a b c	a	1.88 s		400 MHz, C_7D_8
	b	0.91	$^1J = 129$	
	c	0.139	$^1J = 120$	

Compound	Assignment	δ (ppm)	Coupling	Comments
$Cp^*_2Sc^{13}CH_2{}^{13}CH_3$	a	1.035	^1J = 130	400 MHz, -80°C, C_7D_8
a b	b	0.077	^1J = 121	
$Cp^*_2Sc^{13}CH_2{}^{13}CH_2D$	a	0.91	^1J = 129	400 MHz, C_7D_8
a b	b	0.049	^1J = 120	
$Cp^*_2Sc^{13}CH_2{}^{13}CH_2D$	a	1.035	^1J = 130	400 MHz, -80°C, C_7D_8
a b	b	-0.046	^1J = 119	
$Cp^*_2ScCH_2CH_2CH_3$	a	1.88 s	6.6	500 MHz
	b	1.40 t	6.6	
a b c d	c + d	0.86-1.00 m		
$Cp^*_2ScCH_2CH_2CH_3$	a (C_5)	118.60		$^{13}C\{^1H\}$, C_7D_8 400 MHz, -50°C
	a ($(CH_3)_5$)	11.19		
a b c d	b	45.8 (broad)		
	c	22.76		
	d	24.58		

Compound	Assignment	δ (ppm)	Coupling	Comments
$Cp^*_2ScCH_2CH=CH_2$	a	1.90 s		25°C, C_6D_{12}
a b c d	b + D	3.0 d	12.7	
	c	7.15 q	12.7	
	a	1.92 s		-50°C, C_7D_8
	a'	1.80 s		
	b	2.07 d	9.8	
	d	3.93 d	15.6	
	a	1.84 s		90°C, C_7D_8
	b + d	2.86 d	12.7	
$Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$	a	1.77 s		
	b	7.93 d t	5.1, 1.5	
a b	b	7.65 d t	7.2, 1.5	
	b	7.03 t d	7.2, 1.2	
	b	6.58 m		

* Unless otherwise specified, spectra were taken in C_6D_6 at ambient temperature at 90 Mhz. The chemical shifts are reported in relative to TMS or residual protons of the solvent. Coupling constants are reported in Hz.

recorded using Kratos MS25 and Dupont 4592 mass spectrometers. Analyses were performed by Bernhardt Analytical Laboratories or the Caltech Analytical Laboratory. Molecular weights were determined using the vapor phase osmometry technique developed by Signer and described by Clark.[27]

Structure Determination of $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$. Single crystals, grown from a toluene solution at -80°C for two days were mounted in glass capillaries under N_2. Oscillation and Weissenberg photographs indicated orthorhombic symmetry ($a = 16.297(4)$Å, $b = 9.684(3)$Å, $c = 14.486(6)$Å, $V = 2286.3(12)$Å^3, Z = 4). The crystals decompose rapidly with x-ray exposure. After 8--10 hours the reflection intensities begin to decrease, and after 24 hours no diffraction is observed. Intensity data were collected on a locally-modified Syntex $P2_1$ diffractometer with graphite monochromator and MoKα radiation at a fast scan speed (8.37°/min in 2θ); an entire quadrant ($+h, +k, \pm\ell$) to 2θ = 30° was collected in 8.5 hours with θ--2θ scans ($\Delta 2\theta$ = 2.8° plus dispersion) and indicated no observable deterioration. Systematic absences in the intensity data indicated space group $Pna2_1$. The intensities were reduced to F_o^2; the form factors for Sc were corrected for anomalous dispersion.

The coordinates of the scandium atom was derived from the Patterson map, and a series of Fourier maps were used to determine the coordinates of the remaining non-hydrogen atoms. Hydrogen atom positions were determined by assuming idealized geometry and by locating peaks in the difference map.

The pyridyl ligand is disordered and results in the complete superposition of two pyridyl groups of equal population. To model

this, all atoms in the pyridyl group were given full populations, except for the two atoms bound to Sc, which were each modelled as 50% carbon and 50% nitrogen atom. Least-squares refinement of the coordinates of all non-hydrogen atoms with anisotropic Gaussian displacement parameters, U_{ij}'s, an isotropic secondary extinction parameter, and hydrogen atoms with fixed coordinates and isotropic U's ($U = 0.09\text{Å}^2$) resulted in S (goodness--of--fit) $\{\Sigma w[F_o^2-(F_c^2/k)^2]^2/(n-p)\}^{1/2} = 1.74$, R ($\Sigma \mid\mid F_o \mid - \mid F_c \mid\mid / \Sigma \mid F_o \mid$ for $I > 0$) = 0.045, and R' (R for $I > 3\sigma_I$) = 0.036; final shift/error < 0.01. Final atom coordinates and U_{ij}'s are given in Table 3, hydrogen atom coordinates in Table 4, bond lengths in Table 5, and angles in Table 6. The final value of the secondary extinction parameter is $1.55(16)\times10^{-6}$. The atoms numbered 1 and 2 are the pyridyl atoms bound to scandium. Atoms C3-C6 are the remaining atoms (carbons) of the pyridyl ring. C11-C15 and C31-C35 are Cp* inner ring carbons, and C21-C25 and C41-C45 are the methyl groups associated with them, respectively.

Structure determination of $Cp^*_2ScCH_3$. Single crystals, grown from pentane at -80°C for two days, were mounted in glass capillaries under N_2. The crystals were screened by examination of their oscillation photographs and a satisfactory one was carefully centered on a Syntex $P2_1$ diffractometer equipped with a graphite-monochromated MoKα radiation. An orthorhombic cell was found and cell dimensions were obtained from a least-squares fit to the setting angles of 15 reflections (various forms of 6 independent reflections) with $20^\circ<2\theta<26^\circ$. Systematic absences observed in the data of h00, h = 2n + 1; 0k0; k = 2n + 1; and 00l, l = 2n + 1 are

Table 3. Atomic coordinates (x 10^5) and gaussian amplitudes ($Å^2$, x 10^4) for all non-hydrogen atoms of $Cp^*_2Sc(C,N-\eta^2-C_5H_4N)$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Sc	28578(7)	−1816(11)	0	317(6)	415(7)	390(7)	−2(7)	−17(10)	31(11)	374(3)
(1)	17558(39)	−10404(77)	6026(51)	413(44)	490(42)	509(48)	−56(37)	−48(39)	156(40)	471(18)
(2)	18949(43)	1576(79)	10236(54)	376(42)	646(63)	470(49)	42(44)	−50(41)	131(47)	497(21)
C(3)	13564(59)	6826(94)	16781(61)	590(60)	953(72)	552(62)	119(58)	−11(53)	22(54)	698(28)
C(4)	6534(54)	−317(131)	18697(63)	505(61)	1381(94)	630(61)	171(75)	152(51)	36(74)	839(33)
C(5)	5100(52)	−13007(118)	14513(81)	397(55)	1254(93)	891(82)	−228(62)	−113(61)	462(77)	847(35)
C(6)	10543(58)	−17920(90)	8270(62)	540(57)	842(62)	615(62)	−206(54)	−141(53)	143(54)	666(25)
C(11)	30262(46)	4534(77)	−16638(51)	549(56)	541(54)	415(46)	130(43)	15(42)	96(42)	502(21)
C(12)	30997(44)	16736(77)	−11647(54)	452(55)	476(48)	507(51)	−8(41)	−36(44)	132(45)	478(21)
C(13)	23404(45)	19636(70)	−7498(55)	525(56)	432(46)	427(47)	66(45)	−50(42)	85(40)	461(20)
C(14)	17865(49)	9056(86)	−10054(55)	396(51)	558(56)	433(56)	73(52)	−90(44)	101(46)	462(23)
C(15)	22167(46)	−513(76)	−15617(53)	572(56)	433(47)	508(51)	16(52)	−228(49)	−9(47)	504(21)
C(21)	36505(57)	−1082(110)	−23613(63)	767(62)	1111(86)	562(59)	197(71)	195(55)	114(58)	813(29)
C(22)	38246(51)	26819(87)	−11429(67)	617(56)	722(57)	939(69)	−66(50)	50(54)	371(57)	759(25)
C(23)	21350(54)	32221(72)	−1872(65)	889(54)	553(44)	789(84)	234(49)	−57(59)	−18(51)	744(25)
C(24)	8820(50)	8693(99)	−8205(73)	451(57)	1033(69)	925(73)	179(53)	−136(53)	307(63)	803(30)
C(25)	18637(61)	−12926(91)	−20048(67)	1090(79)	722(63)	695(62)	−88(58)	−287(59)	−76(54)	836(28)
C(31)	43661(37)	−7041(67)	828(76)	370(39)	552(47)	525(49)	42(34)	−22(57)	171(61)	482(19)
C(32)	41579(42)	−490(78)	9052(60)	419(45)	537(55)	661(61)	−38(43)	−225(45)	139(56)	539(22)
C(33)	36338(46)	−9461(86)	14017(50)	401(44)	711(57)	326(47)	120(45)	18(41)	153(48)	479(22)
C(34)	35092(43)	−21194(73)	8634(60)	376(46)	462(51)	632(61)	−30(39)	−85(49)	174(48)	490(22)
C(35)	39511(39)	−19737(63)	432(77)	429(40)	472(44)	605(48)	144(36)	−11(65)	51(64)	502(18)
C(41)	50417(47)	−2484(102)	−5893(65)	391(44)	1202(77)	934(65)	67(54)	103(47)	451(67)	842(28)
C(42)	45133(63)	13014(89)	12332(77)	1029(73)	731(63)	1014(76)	−17(60)	−506(67)	45(59)	925(29)
C(43)	33535(60)	−6858(124)	23858(70)	776(65)	1346(100)	543(65)	265(67)	−46(56)	118(63)	888(34)
C(44)	30558(53)	−34019(90)	11543(79)	711(64)	769(62)	1235(85)	−71(53)	−103(61)	412(63)	905(29)
C(45)	40348(59)	−30615(94)	−6777(77)	876(68)	806(65)	1165(90)	314(58)	−150(67)	−142(68)	949(30)

Table 4. Hydrogen atom coodinates (x 10^4) for $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$.

	x	*y*	*z*
H(3)	1507	1571	2015
H(4)	222	398	2302
H(5)	0	−1856	1644
H(6)	933	−2717	483
H(211)	3260	−300	−2951
H(212)	4080	380	−2421
H(213)	3490	−1140	−2171
H(221)	3770	3310	−1641
H(222)	3400	3100	−611
H(223)	4330	2170	−1301
H(231)	2510	3550	79
H(232)	1640	2940	289
H(233)	1760	3820	−581
H(241)	720	1310	−391
H(242)	650	−110	−901
H(243)	560	1310	−1411
H(251)	1770	−2090	−1551
H(252)	1410	−1170	−2341
H(253)	2280	−1770	−2401
H(411)	4880	−10	−1101
H(412)	5410	−1130	−741
H(413)	5400	370	−341
H(421)	4480	1970	819
H(422)	5070	1150	1489
H(423)	4180	1560	1809
H(431)	3780	−1000	2809
H(432)	3100	70	2449
H(433)	2870	−1470	2519
H(441)	2810	−3310	1669
H(442)	3500	−4160	1219
H(443)	2740	−3720	649
H(451)	3530	−3620	−771
H(452)	4220	−2710	−1271
H(453)	4460	−3770	−511

Table 5. Bond lengths for $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$.

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Sc	1	2.162(7)	C11	C12	1.390(11)
	2	2.183(8)		C15	1.414(11)
	C11	2.502(8)		C21	1.533(12)
	C12	2.496(8)	C12	C13	1.403(12)
	C13	2.491(7)		C22	1.533(12)
	C14	2.505(8)	C13	C14	1.414(11)
	C31	2.511(8)		C23	1.504(11)
	C32	2.494(8)	C14	C15	1.414(11)
	C33	2.504(8)		C24	1.498(12)
	C34	2.492(8)	C15	C25	1.480(12)
	C35	2.487(8)			
			C31	C32	1.392(11)
1	2	1.330(10)		C35	1.404(11)
	C6	1.393(12)		C41	1.534(12)
2	C3	1.388(12)	C32	C33	1.414(11)
C3	C4	1.366(14)		C42	1.507(13)
C4	C5	1.390(15)	C33	C34	1.393(11)
C5	C6	1.353(14)		C43	1.518(13)
			C34	C35	1.400(11)
				C44	1.505(12)
			C35	C45	1.490(13)

Table 6. Bond angles for $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$.

Atom	Atom	Atom	Angle (°)
CENT1	Sc	CENT2	142
1	Sc	2	35.7(2)
	2	Sc	71.3(3)
	C5	C6	120.6(8)
2	1	Sc	120.6(8)
	1	sC	73.0(5)
	C3	C4	118.8(8)
C3	C4	C5	120.0(9)
C4	C5	C6	119.5(9)

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C15	C11	C12	108.6(7)	C35	C31	C32	108.5(7)
		C21	124.3(7)			C41	124.8(7)
C12		C21	126.0(7)	C32		C41	125.9(7)
C11	C12	C13	108.5(7)	C31	C32	C33	107.6(7)
		C22	128.2(7)			C42	124.9(7)
C13		C22	122.8(7)	C33		C42	127.2(7)
C12	C13	C14	107.8(7)	C32	C33	C34	107.7(7)
		C23	126.1(7)			C44	123.9(7)
C14		C23	125.9(7)	C34		C44	128.1(7)
C13	C14	C15	107.9(7)	C33	C34	C35	108.6(7)
		C24	126.7(7)			C44	126.0(7)
C15		C24	125.0(7)	C35		C44	125.1(7)
C14	C15	C11	107.1(7)	C34	C35	C31	107.6(7)
		C25	126.0(7)			C45	124.9(7)
C11		C25	125.7(7)	C31		C45	127.1(7)

unique for the space group $P2_12_12_1$. Five octants of data (hkl, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, $h\bar{k}l$ and $\bar{h}\bar{k}\bar{l}$) were collected with $4^o<2\theta<40^o$ and one octant, hkl, with $40^o<2\theta<50^o$. The data were merged to give 2076 independent reflections, of which 1859 had $F_o>0$ and 1143 $F_o^2>3\sigma(F_o^2)$. Three check reflections monitored every 97 reflections showed a linear decay of 1.5% in F over 230 hours required to collect the data. The data were corrected for this decay, Lorentz and polarization factors were applied and a Wilson plot was used to put the data on an approximately absolute scale. Variances, $\sigma^2(I)$, were assigned intensities on the basis of counting statistics plus an additional term, $(0.02\ I)^2$, to account for additional errors proportional to the intensity. A Patterson map gave the scandium coordinates and successive structure factor-Fourier calculations located the remaining atoms. Many cycles of least squares refinement, first with isotropic and then anisotropic thermal parameters finally converged with R = 0.15 for all reflections with $F_o>0$ and 0.112 for reflections with $F_o^2>3\ (F_o^2)$. Hydrogen atoms were introduced, based on difference maps calculated in the planes where they were expected. These maps were unequivocal, as the methyl carbon atoms have very large anisotropic temperature factors, but in most cases 3 reasonable locations for the hydrogen atoms were obtained. These were optimized to tetrahedral geometry with a C-H distance of 0.95 Å and the hydrogen atoms were included in subsequent calculations as constant contribu-

tions to the structure factors, with isotropic thermal parameters, B, of 10.0 $Å^2$. Six more cycles of least squares, the hydrogen atoms being repositioned two times, concluded the refinement; the final R values are 0.113 for all data and 0.72 for the strong data. The goodness of fit (S) is 2.98. In the final least squares cycle no parameter shifted more than one-half its standard deviation. A final difference map showed no excursion greater than ± 0.44 e/$Å^3$. Crystal data are given in Table 7. Hydrogen atom coordinates given in Table 8, and final heavy atom coordinates and U_{ij}'s are given in Table 9. Bond lengths and angles are given in Table 10. Atoms numbered C1-C5 and C11-C15 are Cp* inner ring carbons, and atoms numbered C6-C10 and C16-C20 are the methyl groups attached to them, respectively. C21 is the methyl ligand bound to scandium.

Preparation of Cp^*_2ScCl. $ScCl_3(THF)_3$ (10.0 g, 27 mmol), LiCp* (9.0 g, 63 mmol) and 250 mL of xylene were placed in a 500 mL round bottom flask equipped with a reflux condenser. The slurry was refluxed for one day and approximately 30 mL of solvent was then distilled from the reaction flask. The slurry was refluxed for a second day and 30 mL of solvent was again removed. The reaction was refluxed for a third day and all of the volatiles removed in vacuo. The remaining solid was transferred to a sublimator. Bright yellow crystalline Cp^*_2ScCl (8.0 g, 80%) was collected by sublimation for four days at 120 °C (10^{-5} torr). The molec-

Table 7. Crystal data for $Cp^*_2ScCH_3$.

formula: Sc C_{21} H_{33} f. wt. 330.45

Space Group $P2_12_12_1$(#19) V = 2033(1) $Å^3$

z = 4

a = 8.502(2) Å

b = 11.095(4) Å (T = 21°C) ρ_c = 1.079(1) g/cc

c = 21.554(7) Å

λ MoKᾱ = 0.71073 Å μ(MoKᾱ) = 3.65 cm^{-1}

F(000) = 720.0 e μr_{max} = 0.12

Crystal size 0.24 x 0.34 x 0.51 mm

Table 8. Hydrogen atom coordinates (x 10^4) of $Cp^*_2ScCH_3$.

All Hydrogen atoms were assigned isotropic thermal parameters, B, of 10.0 $Å^2$. They are numbered according to the carbon atom to which they are attached.

Atom	x	y	z	Atom	x	y	z
H61	-1840	-551	964	H161	-1166	3067	1054
H62	-1896	-1647	512	H162	-2248	2262	1465
H63	-1820	-339	249	H163	-1505	1738	862
H71	1446	905	-333	H171	2824	3881	1291
H72	28	79	-504	H172	1048	4229	1293
H73	1717	-258	-725	H173	1723	3430	761
H81	4522	-94	-114	H181	4735	1756	2134
H82	3997	-1245	-473	H182	3932	2639	2598
H83	5070	-1362	110	H183	4286	3054	1922
H91	4743	-2406	854	H191	3197	-119	2620
H92	3650	-2906	1374	H192	1473	-510	2762
H93	4463	-1657	1455	H193	2206	592	3106
H101	845	-3150	1475	H201	-984	-545	2245
H102	-663	-2354	1511	H202	-2039	291	1839
H103	786	-2054	1926	H203	-1706	622	2529
H211	5118	967	982				
H212	4215	2141	808				
H213	4340	1091	330				

Table 9. Final atomic coordinates ($\times 10^4$) and gaussian amplitudes ($\times 10^3$) for $Cp^*_2ScCH_3$.

Atom	x [a]	y	z	Ueq [b]
Sc	2029(2)	495(1)	1131(1)	53(0.3)
C1	249(8)	-913(8)	579(6)	72(3)
C2	1362(17)	-602(10)	175(4)	78(3)
C3	2718(14)	-1018(11)	353(6)	94(4)
C4	2615(17)	-1597(9)	867(7)	100(4)
C5	1060(19)	-1602(9)	1061(5)	90(4)
C6	-1500(11)	-856(14)	576(10)	313(11)
C7	1113(29)	100(10)	-404(5)	334(10)
C8	4244(19)	-919(13)	-79(8)	241(7)
C9	4009(22)	-2203(13)	1168(11)	315(10)
C10	451(38)	-2361(14)	1537(6)	367(11)
C11	65(11)	1859(10)	1569(5)	82(3)
C12	1416(13)	2489(7)	1568(4)	72(3)
C13	2458(10)	1959(12)	1982(5)	84(4)
C14	1604(17)	951(10)	2239(4)	93(4)
C15	169(15)	977(9)	1965(6)	92(4)
C16	-1359(12)	2274(10)	1200(6)	155(4)
C17	1792(14)	3624(8)	1190(5)	151(4)
C18	4001(14)	2394(15)	2178(6)	218(6)
C19	2175(26)	151(12)	2729(4)	284(9)
C20	-1291(15)	263(11)	2165(6)	183(5)
C21	4259(13)	1293(9)	757(5)	156(4)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sc	46(1)	57(1)	57(1)	-3(1)	1(1)	-10(1)
C1	30(5)	70(7)	116(8)	1(4)	3(6)	-50(6)
C2	113(8)	66(6)	56(6)	-22(7)	-31(6)	12(6)
C3	77(9)	89(9)	116(9)	-3(7)	11(9)	-55(7)
C4	128(12)	50(6)	123(10)	12(7)	-77(10)	4(6)
C5	157(10)	67(7)	47(6)	-62(8)	29(8)	-1(6)
C6	58(7)	289(20)	594(31)	43(9)	-73(11)	-358(23)
C7	750(44)	153(12)	100(8)	-187(20)	-131(16)	4(9)
C8	189(13)	200(16)	334(19)	-73(12)	155(15)	-160(15)
C9	354(23)	114(12)	477(30)	137(15)	-270(25)	-79(17)
C10	843(52)	130(11)	128(10)	-179(22)	193(21)	-52(9)
C11	63(6)	75(7)	109(8)	0(7)	-1(6)	-23(7)
C12	104(8)	49(6)	62(6)	-12(6)	19(6)	-16(5)
C13	46(7)	133(10)	71(6)	8(6)	-17(5)	-54(7)
C14	126(11)	98(9)	54(6)	51(8)	-14(6)	-3(6)
C15	121(10)	65(8)	89(8)	-4(7)	61(8)	-6(6)
C16	111(8)	151(10)	204(11)	58(7)	-53(9)	-83(10)
C17	217(12)	72(6)	163(9)	9(8)	86(11)	11(7)
C18	104(10)	344(22)	206(13)	16(12)	-37(9)	-192(15)
C19	610(33)	185(13)	56(6)	182(20)	-40(13)	0(7)
C20	220(13)	132(10)	198(11)	-70(10)	136(11)	-78(9)
C21	125(9)	162(10)	180(10)	-69(9)	88(8)	-87(9)

Table 10. Bond lengths (Å) and angles (°) for $Cp^*_2ScCH_3$.

Atom	Atom	Dist.(Å)	Atom	Atom	Atom	Angle(°)
Sc	C1	2.480(10)	C2	C1	C5	105.4(9)
	C2	2.460(11)			C6	134.1(10)
	C3	2.444(13)	C5		C6	119.8(10)
	C4	2.441(13)	C1	C2	C3	110.1(10)
	C5	2.473(12)			C7	125.7(11)
	C11	2.443(10)	C3		C7	124.2(11)
	C12	2.460(9)	C2	C3	C4	111.9(12)
	C13	2.476(11)			C8	121.5(11)
	C14	2.467(11)	C4		C8	126.3(12)
	C15	2.452(12)	C3	C4	C5	109.1(12)
C1	C2	1.333(15)			C9	122.7(13)
	C5	1.463(15)	C5		C9	128.2(13)
	C6	1.488(18)	C4	C5	C1	103.5(10)
C2	C3	1.300(17)			C10	124.5(13)
	C7	1.485(19)	C1		C10	130.5(12)
C3	C4	1.284(18)				
	C8	1.601(20)	C12	C11	C15	109.5(10)
C4	C5	1.386(18)			C16	121.5(9)
	C9	1.509(23)	C15		C16	128.6(10)
C5	C10	1.425(24)	C11	C12	C13	108.9(9)
C11	C12	1.344(14)			C17	127.2(9)
	C15	1.302(15)	C13		C17	123.8(9)
	C16	1.520(15)	C12	C13	C14	104.7(9)
C12	C13	1.388(14)			C18	128.3(10)
	C17	1.533(14)	C14		C18	126.6(10)
C13	C14	1.444(16)	C13	C14	C15	105.6(10)
	C18	1.461(17)			C19	125.5(11)
C14	C15	1.356(16)	C15		C19	128.8(11)
	C19	1.462(19)				
C15	C20	1.534(17)				
Sc	C21	2.243(11)	C14	C15	C11	111.3(11)
					C20	126.5(11)
			C11		C20	121.2(10)
Sc-Cp*(1) centroid		2.173(12)	Cp*1	Sc	Cp*2	144.6(10)
Sc-Cp*(2) centroid		2.169(11)	Cp*1	Sc	C21	106.6(8)
			Cp*2	Sc	C21	108.9(8)

ular weight in benzene was 365 g/mole (350 calculated for a monomer). IR data (cm^{-1}): 2715(w), 1030(m), 800(m), 430(s), 360(s). Anal. calc. for $C_{20}H_{30}ClSc$: C, 68.47; H, 8.77; Cl, 10.10. Found: C, 68.05; H, 8.77; Cl, 10.12.

Preparation of $Cp^*_2ScCH_3$. Cp^*_2ScCl (5.0 g, 14 mmol) was dissolved in 75 mL of toluene. $LiCH_3$ (8.01 mL, 1.78 M in Et_2O) was slowly added to the solution with stirring. The reaction was stirred for 30 minutes and the solvent removed in vacuo. Approximately 30 mL of petroleum ether was distilled onto the solid and the resulting slurry was filtered. The solid was washed with 10 mL of petroleum ether twice. The filtrate and washings were combined and concentrated to 10 mL. The solution was cooled to -78 °C, precipitating the pale yellow product, $Cp^*_2ScCH_3$. The product was isolated by cold filtration (2.6 g, 55%). $Cp^*_2ScCH_3$ was stored at -10 °C to prevent decomposition. The molecular weight in cyclohexane was 324 g/mole (331 calculated for a monomer). IR data (cm^{-1}): 2730(w), 1490(m), 1114(s), 1028(s), 800(w), 605(m), 580(m), 420(vs, br). Anal. calc. for $C_{21}H_{33}Sc$: C, 76.33; H, 10.07. Found: C, 76.01; H, 9.98.

Preparation of $Cp^*_2ScCH_2D$ and $Cp^*_2Sc^{13}CH_3$. These compounds were prepared in a manner similar to that described for $Cp^*_2ScCH_3$, except $LiCH_2D$ and $Li^{13}CH_3$, respectively, were used in place of $LiCH_3$.

Preparation of $Cp^*_2Sc(THF)CH_3$. $Cp^*_2ScCH_3$ (1.0 g, 3.0 mmol) was dissolved in approximately 15 mL of THF and the THF removed in vacuo. Five mL of petroleum ether was added to the resulting solid and the solution cooled to -78 °C, precipitating a solid. This slurry was filtered to give a pale yellow product (0.99 g, 81%) IR data (cm^{-1}): 2710(w), 1490(m), 1340(m), 1295(w), 1242(w), 1100(s), 1020(s), 922(m), 865(s), 670(m), 570(m), 460(m), 430(s), 340(s). Anal. calc. for $C_{25}H_{37}OSc$: C, 74.59; H, 10.27. Found: C, 74.53; H, 10.17.

Preparation of $Cp^*_2ScCH_2C_6H_5$. Cp^*_2ScCl (2.0 g, 5.7 mmol) was dissolved in 20 mL of toluene. A solution of 0.830 g (6.3 mmol) of $KCH_2C_6H_5$ dissolved in 20 mL of cold THF was added to the stirred Cp^*_2ScCl solution slowly via cannula. After addition of the benzylpotassium solution was complete, the solvent was removed in vacuo, followed by addition of 20 mL of petroleum ether. The resulting suspension was filtered to give a yellow solution and a white solid. The solid was washed with two 10 mL portions of petroleum ether and the combined petroleum ether solutions were concentrated to 5 mL. Cooling the solution to -78 °C caused the bright yellow $Cp^*_2ScCH_2C_6H_5$ to precipitate (1.34 g, 58%). $Cp^*_2ScCH_2C_6H_5$ was stored at -10°C to prevent decomposition. The molecular weight in benzene was found to be 460 g/mole (407 calculated for a monomer). IR data (cm^{-1}): 3050(w), 2710(w), 1595(s), 1490(s), 1200(s),

1030(m), 935(m), 870(w), 790(m), 740(s), 705(s), 660(w). Anal. calc. for $C_{27}H_{37}Sc$: C, 79.76; H, 9.17. Found: C, 79.67; H, 9.12.

Preparation of $Cp^*_2Sc\text{-}C_6H_5$. Cp^*_2ScCl (2.5 g, 7.6 mmol) was dissolved in 20 mL of petroleum ether. LiC_6H_5 (3.11 mL, 2.4 M in a cyclohexane-Et_2O solution) was added slowly to the petroleum ether solution, and the reaction mixture stirred for 30 minutes. All of the solvent was removed in vacuo and 20 mL of petroleum ether was added. The solution was filtered and the resulting solid washed twice with 10 mL portions of petroleum ether. The filtrate and washings were combined and concentrated to 5 mL. On cooling to -78 ^oC the pale yellow product precipitated and was collected by filtration (1.71 g, 60%). IR data (cm^{-1}): 3430(w), 2730(w), 1590(w), 1563(w), 1485(w), 1312(w), 1233(w), 1165(w), 1067(m), 1025(m), 983(w), 738(w), 722(s), 708(s), 462(s), 418(s). Anal. Calc. for $C_{26}H_{35}Sc$: C, 79.56; H, 8.99. Found: C, 79.58; H, 8.77.

Preparation of $Cp^*_2Sc\text{-}C_6H_4CH_3$-o, -m, -p. The synthesis of $Cp^*_2Sc\text{-}C_6H_4CH_3$-p is described; the -o and -m isomers are prepared in the same manner, except the appropriate tolyllithium reagent is substituted for $LiC_6H_4CH_3$-p. Cp^*_2ScCl (0.420 g, 1.2 mmol) reacted with $LiC_6H_4CH_3$-p (0.18 g, 1.8 mmol) at room temperature in toluene solution (15 mL). After 12 hours the toluene was removed and replaced with 10 mL

of petroleum ether. The petroleum ether solution was filtered and the resulting solid washed twice with petroleum ether. The combined filtrate and washings were concentrated to ca. three mL, and cooled to -78°C. The off-white product was isolated by filtration of the cold petroleum ether slurry (0.285 g, 59%). IR data (cm^{-1}): 2715(w), 1578(w), 1300(w), 1252(w), 1222(m), 1208(w), 1160(w), 1140(w), 1079(m), 1053(w), 1030(s), 1016(s), 793(w), 774(s), 720(w), 549(m), 480(s), 417(s). Anal. calc. for $C_{27}H_{37}Sc$: C, 79.77; H, 9.17. Found: C, 79.79; H, 9.08.

Preparation of $Cp^*_2Sc(THF)H$. $Cp^*_2ScCH_3$ (1.0 g, 3.0 mmol) was dissolved on 20 mL of THF. One atmosphere of hydrogen was admitted to the reaction vessel and the solution stirred for five hours. The THF was removed in vacuo and replaced with seven mL of petroleum ether. This solution was cooled to -78°C, causing the pale yellow $Cp^*_2Sc(THF)H$ to precipitate. The product was isolated by filtration (0.82 g, 70%). The molecular weight in cyclohexane was found to be 408 g/mole (388 calculated for a monomer). IR data (cm^{-1}): 2710(w), 1390(s), 1155(m), 1140(m), 1020(s), 855(s), 730(s), 655(m), 510(m), 365(m). Anal. calc. for $C_{24}H_{39}OSc$: C, 74.19; H, 10.12. Found: C, 74.08; H, 10.14.

Preparation of $Cp^*_2ScCH_2CH_3$. A 50 mL thick walled glass bomb was charged with $Cp^*_2ScCH_3$ (0.280 g, 0.85 mmol), 10 mL of toluene and four atmospheres of H_2. This toluene

solution was stirred for ten minutes at room temperature and then cooled to -78°C. The hydrogen was removed and one equivalent of ethylene (375 torr in 42.2 mL) was condensed into the cold bomb (-78°C). The bomb was allowed to come to room temperature and the toluene solution transferred to a flask. The toluene was removed in vacuo and replaced with 10 mL of petroleum ether. This solution was filtered and the filtrate concentrated to ca. three mL. Cooling this solution to -78°C precipitates a yellow solid, which was isolated by filtration (0.160 g, 55%). IR data (cm^{-1}): 2714(m), 2593(m), 2503(m), 2440(m),1493(s), 1172(w), 1066(m), 1025(s), 973(m), 844(s), 807(m), 722(w), 660(m), 618(m), 568(s), 480(s). Anal. calc. for $C_{22}H_{35}Sc$: C, 76.71; H, 10.24. Found: C, 76.66; H, 10.22.

Preparation of $Cp^*_2Sc^{13}CH_2{}^{13}CH_3$ and $Cp^*_2Sc^{13}CH_2{}^{13}CH_2D$. $Cp^*_2Sc^{13}CH_2{}^{13}CH_3$ was synthesized by substituting $^{13}C_2H_4$ for nonlabeled ethylene in the procedure described for $Cp^*_2ScCH_2CH_3$. $Cp^*_2Sc^{13}CH_2{}^{13}CH_2D$ was prepared by substituting labeled ethylene for unlabeled ethylene and using deuterium rather than hydrogen in the described synthesis of $Cp^*_2ScCH_2CH_3$, and the reaction time for deuterium with $Cp^*_2ScCH_3$ was five minutes.

Preparation of $Cp^*_2ScCH_2CH_2CH_3$. We were unable to prepare this compound in a manner analogous to the preparation of $Cp^*_2ScCH_2CH_3$. $Cp^*_2ScCH_2CH_2CH_3$ is too soluble in non-re-

active solvents to allow its isolation by cooling a concentrated solution. In a typical experiment 500 mg of $Cp^*_2ScCH_3$ (1.5 mmol) and 10 mL of toluene were loaded into a 50 mL glass bomb. The bomb was charged with 4 atm of H_2 and the solution stirred for 10 minutes. The toluene solution was cooled to -78°C and the H_2 removed <u>in vacuo</u>. Propene (1.5 mmol) was added to the cold toluene solution, and the bomb allowed to warm to room temperature slowly. The toluene was removed <u>in vacuo</u> and replaced with 5 mL of petroleum ether. This solution was cloudy on some occasions (due to a small amount of H_2O in the H_2), when this occurred the solution was filtered. The petroleum ether was removed <u>in vacuo</u> and the resulting solid was the product (90-95% pure, 440 mg, 80% yield). The 500 MHz ^1H NMR spectrum of $Cp^*_2ScCH_2CH_2CH_3$ shows a single Cp* resonance (1.86 ppm, 30H), a triplet for the α-CH_2 group (1.40 ppm, J = 6.6 Hz, 2H) and two overlapping multiplets for the β-CH_2 and CH_3 groups (0.86-1.00 ppm, 5H). The ^{13}C spectrum of this compound is reported in Table 2. Satisfactory C,H analysis were not obtained. IR data (cm^{-1}): 2735(w), 1306(w), 1160(br, w), 1060(sh), 1028(s), 862(w), 805(w), 750(m), 723(m), 666(s), 618(m), 580(m), 505(m), 412(vs).

<u>Preparation of $Cp^*_2Sc(\eta^3$-$CH_2CH{=}CH_2)$.</u> This compound was prepared in a manner analogous to $Cp^*_2ScCH_2CH_3$, except allene was used in place of ethylene; 0.220 g of Cp^*_2ScCl yielded 0.160 g of $Cp^*_2ScCH_2CH{=}CH_2$ (67%). IR data (cm^{-1}):

3090(w), 2725(w), 1554(s), 1258(s), 1155(w), 1085(w), 1028(s), 785(s), 755(m), 705(s), 635(sh), 618(sh), 595(m). Anal. calc. for $C_{23}H_{35}Sc$: C, 77.49; H, 9.90. Found: C, 77.25; H, 10.00.

Preparation of $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$. $Cp^*_2ScCH_3$ (1.0 g, 3.0 mmol) was dissolved in 25 mL of benzene and 0.25 mL (3.1 mmol) of pyridine was added. The solution was heated to reflux for 30 minutes and the solvent removed in vacuo. The product was dissolved in 5 mL of Et_2O and the solution cooled to -78°C giving the crystalline product, which was isolated by filtration and washed once with -78°C Et_2O (0.71 g, 60%). IR data (cm^{-1}): 2720(w), 1573(s), 1535(w), 1414(m), 1252(w), 1216(s), 1150(w), 1020(w), 985(w), 757(s), 720(s), 405(m). Anal. calc. for $C_{25}H_{34}NSc$: C, 76.31; H, 8.71; N, 3.56. Found: C, 76.53; H, 8.69; N, 3.38.

H_2 Uptake by $Cp^*_2ScCH_2C_6H_5$ (eq 7). $Cp^*_2ScCH_2C_6H_5$ (0.607 g, 1.50 mmol) was dissolved in ten mL of benzene in a 50 mL thick walled glass bomb. The bomb was then charged with 2.65 mmol of H_2 and the solution stirred for one hour. The benzene solution was cooled to 10°C and the amount of unused H_2 measured with a Toepler pump. Initially, 1.26 mmol of H_2 was collected, indicating that $Cp^*_2ScCH_2C_6H_5$ had taken up 0.93 equivalents of H_2. The solution continued to give off hydrogen slowly, well after it should have been degassed. This is most likely due to a secondary reaction of

Cp^*_2ScH with C_6H_6, which yields H_2 (vide infra). This secondary reaction may also account for the low (0.93 equivalents rather than 1.0 equivalents) level of H_2 uptake observed.

Determination of the Half-life of the Reaction of $Cp^*_2ScCH_3$ with H_2. $Cp^*_2ScCH_3$ (60 mg, 0.018 mmol) was dissolved in two mL of toluene in a 15 mL thick walled glass vessel and the solution cooled to -78°C. The solution was stirred rapidly as 2 atm of H_2 was put over the solution. The stirring was continued for 7 minutes and all of the gas not condensed at -196°C (H_2 and CH_4) was removed from the reaction vessel by Toepler pump. The H_2 was removed from the gas by passage of the gas over a heated CuO catalyst and then through a -196°C trap, leaving only CH_4 in the gas phase. The amount of methane was 0.014 ± 0.0005 mmol. Thus 77% of the original $Cp^*_2ScCH_3$ reacted to give CH_4, indicating that the half-life of the reaction is 4-5 minutes. The NMR spectrum of the reaction solution after removal of H_2 shows that $Cp^*_2ScCH_3$ accounts for 25% of the scandium species present (Cp^*_2ScH and $Cp^*_2Sc\text{-}C_6H_4CH_3$ account for 75%), consistent with the Toepler experiment.

$Cp^*_2ScH + CH_3I$. A thick walled glass bomb was charged with $Cp^*_2ScCH_2C_6H_5$ (0.050 g, 0.12 mmol), three mL of toluene and four atmospheres of H_2. The solution was stirred for one hour and the excess H_2 removed. CH_3I (0.36 mmol) was

condensed into the bomb at -196°C. As the toluene solution was warmed to room temperature gas was evolved, which was transferred to a gas bulb with the Toepler pump. Mass spectral analysis showed the gas was methane. The toluene solution was taken to dryness and the resulting yellow solid identified as Cp^*_2ScI by NMR analysis.

$\underline{Cp^*_2Sc(THF)H + CH_3I.}$ $Cp^*_2Sc(THF)H$ (0.020 g, 0.052 mmol) was transferred into an NMR tube mounted on a ground glass joint and fitted with a teflon needle valve adapter. d_6-benzene (ca. 0.4 mL) was distilled into the tube, followed by 0.052 mmol of CH_3I and the tube was sealed with a torch. Immediately upon warming the tube to room temperature a reaction occurred, yielding only $Cp^*_2Sc(THF)I$ and CH_4 (^1H NMR).

$\underline{Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N) + D_2.}$ An NMR tube was prepared as described above with 0.025 g $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$ (0.064 mmol) dissolved in 0.35 mL of d_{12}-cyclohexane. Prior to sealing, the entire tube was cooled to 77 K and 700 torr of D_2 admitted to the tube and it was sealed. After two days the resonance assigned to the ortho proton is no longer observed, while the other protons are observed at the same ppm and relative intensity as in the perprotio analogue.

$\underline{Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N) + d_5\text{-pyridine.}}$ A sealed NMR tube was prepared with 0.025 g $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$ (0.064 mmol) and 0.026 mL d_5-pyridine (0.32 mmol, 5 equivalents) dis-

solved in 0.35 mL C_6D_6. After two days at room temperature the pridyl ligand was replaced by d_1-pyridine in the ^1H NMR spectrum, while the Cp* resonance remained unchanged.

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15. If the averaging is simple, the following equation should hold:

$$\delta_{observed} = \frac{[Cp^*_2ScH](\delta_{hydride}) + 2[H_2](\delta_{hydrogen})}{[Cp^*_2ScH] + 2[H_2]}$$

where the observed chemical shift in toluene-d_8 is 6.65 ppm, $[Cp^*_2ScH]$ is 0.13(2) M and $[H_2]$ is 0.013(3) M.

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C-H Bond Activation and σ-Bond Metathesis by Permethylscandocene Complexes.

Introduction

The carbon-hydrogen bond is the most common unit in carbon based molecules, thus it is no surprise that activation of C-H bonds is a very active area of study for organometallic chemists. Several organometallic compounds have been reported that will activate C-H bonds homogeneously, and the mechanisms of these reactions are of great interest. Selective activation of C-H bonds could convert simple hydrocarbons into valuable feedstocks for industrial processes. These reactions are also of interest because the C-H bond is one of the strongest in organic compounds and has historically been the most inert, making selective functionalization of these bonds a great challenge.

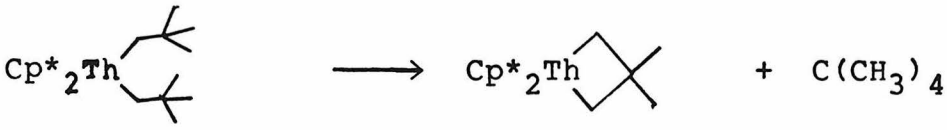
The mechanisms of C-H activation by group VIII metal complexes are fairly well understood.[1] The active metal species is generally electron rich and coordinatively unsaturated, and the C-H bond reacts by oxidative addition to the metal center. This reaction is often followed by reductive elimination of the newly formed hydride ligand with a leaving group (either intra- or intermolecularly).[2] This mechanism works well for some low valent transition metal complexes with readily accessible higher oxidation states;[3] however, many d^0 (oxidatively inert) complexes also activate C-H bonds.[4] In every case the d^0 complex

possesses a leaving group that is replaced by the carbon of the activated C-H bond (eq 1).

$$M\text{-}R + C\text{-}H \longrightarrow M\text{-}C + R\text{-}H \qquad (1)$$

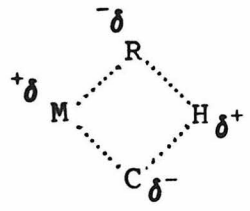
The mechanisms of these reactions of d^0 complexes have not been investigated as intensively as their group VIII counterparts.

The mechanistic studies of C-H bond activation by d^0 metals have centered largely on reactions for which an intramolecular C-H bond is activated (eg. eq 2).[5]



(2)

Labeling studies show that the alkyl leaving group reacts directly with the C-H bond being activated,[5, 6] arguing against both homolytic bond cleavage and activation of a different C-H bond, followed by rearrangement to the observed products (eg. for reaction 2, the mechanism could have involved initial α-abstraction, rather than direct gamma-C-H activation). Activation parameters obtained from kinetic measurements indicate that the transition states for these intramolecular reactions are highly ordered.[4, 5] Based on these results, a four-centered transition state, (4-C), has been proposed.



(4-C)

Unfortunately, experiments to directly determine the degree of charge localization in the transition state (the magnitude of δ) have not been reported. Moreover, very little is known about the mechanisms of intermolecular C-H bond activation by these complexes. The transition states are thought to be similar to (4-C) based on analogy.

Using Cp^*_2ScR (R = hydride, alkyl, aryl) we have studied the inter- and intramolecular activation of C-H bonds by d^0 metal complexes. These complexes react readily with arene and alkane C-H bonds as well as the CH_3 groups of their own Cp* ligands. Examination of the kinetics and product distributions of these reactions allows a fairly detailed picture of the transition state of C-H activation reactions to be drawn.

These C-H bond activation reactions are part of a broad class of reactions we term "σ-bond metathesis" (eq 3).

$$Cp^*_2Sc\text{-}R + A\text{-}B \longrightarrow Cp^*_2Sc\text{-}A + R\text{-}B \qquad (3)$$

R = hydride, alkyl, aryl; A-B = H_2, C-H, C-X, X-C;
X = halide

A general mechanism is proposed for this metathesis reaction. In all cases we have found, the rate of this reaction is strongly dependent on the type of bonding between A and B (s, sp, sp^2, or sp^3) and the orientation of A-B in the transition state.

RESULTS AND DISCUSSION

H/D Exchange Reactions Catalyzed by Permethylscandocenehydride Complexes. H/D exchange reactions involving C-H bonds are one of the most studied forms of C-H activation. Both hetero- and homogeneous metal complexes catalyze this reaction, with aromatic C-H bonds generally being the most reactive.[1(b), 7] The higher reactivity of aryl C-H bonds is usually attributed to prior coordination of the arene's cloud.[8]

Permethylscandocene hydride complexes catalyze H/D exchange for a diverse group of C-H bonds. As with other catalyst, the H/D exchange reaction is rapid for arene C-H bonds. H/D exchange between Cp^*_2ScH and $C_6D_5CD_3$ is slow at low temperatures; no exchange is observed over a period of hours at -60°C. However, when Cp^*_2ScD is dissolved in C_6H_6 at 25°C and one equivalent of CH_3I (based on scandium) is added to this solution after 5 minutes, the product methane is >95% CH_4 (500 MHz NMR), indicating that the exchange reaction was complete or near complete, (eq 4).

$$Cp^*_2ScD + C_6H_6 \xrightarrow[25^oC]{5\ min.} \xrightarrow{CH_3I} Cp^*_2ScI + C_6D_5H + CH_4 \quad (4)$$

Repeating this reaction in C_6D_6 yields only CH_3D. A upper limit for the half-life of the exchange reaction of one minute is thus established at 25°C. $Cp^*_2Sc(THF)H$ also cat-

alyzes this exchange, but at a much slower rate. Above 50°C, the THF hydride complex exchanges rapidly with arene solvent; however, for comparison to the base free hydride, the exchange was examined at 25°C. When a C_6D_6 solution of $Cp^*_2Sc(THF)H$ is let stand at room temperature for 1.5 hours and then treated with CH_3I, only CH_4 is observed by NMR (<5% CH_3D), indicating that very little exchange has occurred (eq 5).

$$Cp^*_2Sc(THF)H + C_6D_6 \xrightarrow[25^oC]{90\ min.} \xrightarrow{CH_3I} Cp^*_2Sc(THF)I + CH_4 \quad (5)$$

A lower limit for the half-life of this reaction is 1000 minutes. The large difference in rate for Cp^*_2ScH <u>versus</u> $Cp^*_2Sc(THF)H$ suggests that the THF ligand must dissociate prior to H/D exchange. A large difference in rate was also observed in the reactions of Cp^*_2ScH and $Cp^*_2Sc(THF)H$ with H_2 (vide supra).

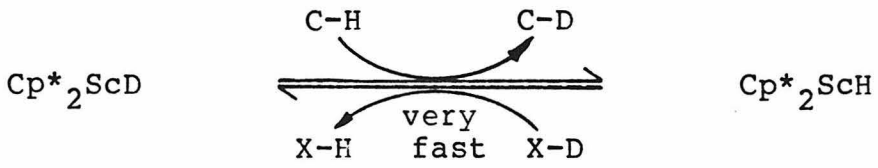
When toluene is the organic substrate used for H/D exchange, both positional preference (ortho, meta or para to CH_3) and the relative rates of aryl <u>versus</u> alkyl exchange can be measured. The positional preference for exchange was examined by reacting toluene-<u>d</u>$_8$ with H_2 (Cp^*_2ScH catalyst) (eq 6).

$$C_7D_8 \xrightarrow[4\ atm\ H_2]{[Cp^*_2ScH]} C_7D_nH_{8-n} \quad (6)$$

In the initial stages of this exchange reaction (2-3 turnovers), the meta and para positions show equal rates of exchange, while the ortho exchange is very slow. Heating the reaction to 80°C for 48 hours leads to an unchanging ratio of protons ortho:meta:para, this thermodynamic ratio is 39:41:20, respectively (500 Mhz ^{1}H NMR). All other H/D exchange catalysts show less than statistical exchange ortho to the methyl group.[7, 9] H/D exchange into the methyl group also occurs but has a rate 60-70 times slower than that observed for aryl C-H exchange. Although continued heating does not change the ratio of protons in the different ring positions, it does increase the degree of H/D exchange into the toluene methyl group. The ratio of aryl *versus* methyl exchange becomes richer in methyl exchange than statistically predicted (5:3 for $C_6D_5CD_3$), and eventually reaches thermodynamic equilibrium at 5.0:4.0 (aryl:methyl).

Most of the H/D exchange experiments were monitored by ^{1}H NMR, and the progress of the exchange measured by the decrease in intensity of the resonances due to the exchanging organic substrate relative to a nonexchanging reference (*eg.* cyclohexane or cyclooctane). For this effect to be marked a significant amount of deuterium must be exchanged into the substrate, which is difficult to do if the only deuterium source is D_2. Only 5-10 equivalents (based on Cp^*_2ScH) can be conveniently put into an NMR tube. For this reason all

of the H/D exchange reactions were done in C_6D_6 solvent; this gave each experiment nearly 400 equivalents of deuterium, in the solvent alone. The rates of H/D exchange into all of the substrates other than arenes are slow enough that substrate H/D exchange is rate limiting rather than regeneration of the catalyst. To prevent decomposition of the catalysts all of these experiments were done with four atmospheres of D_2 over the reaction solutions. Under these conditions H/D exchange proceeds as shown in Scheme 1.



X = D, aryl

Scheme 1

Permethylscandocenehydride complexes catalyze intramolecular H/D exchange for the Cp* ligands and the α-position of the THF ligands at 80°C. The β-position of THF is not exchanged at this temperature over a period of many days. The methyl groups of Cp^*_2ScH exchange at a rate of roughly 2 turnovers/hour (80°C), while the Cp* ligands of the THF adduct, $Cp^*_2Sc(THF)H$, show a slower rate of exchange of 1 turnover/hour. Since free and coordinated THF are in rapid equilibrium, $Cp^*_2Sc(THF)H$ acts as a catalyst for the intermolecular H/D exchange of the α-positions of THF, even

though this exchange is almost certainly intramolecular. In an experiment where ten equivalents of THF is added to Cp^*_2ScH, the rate of H/D exchange into THF is 2 turnovers/hour, while that of the Cp* methyl groups is only 1 turnover/hour.

Intermolecular H/D exchange is observed for several 1^o C-H bonds. CH_4, $Si(CH_3)_4$, $\underline{CH}_3CH_2\underline{CH}_3$ and $P(CH_3)_3$ [10] readily undergo H/D exchange promoted by Cp^*_2ScH. $Cp^*_2Sc(THF)H$ also catalyzes this exchange for these substrates, but in all cases the rate is much lower than that observed for Cp^*_2ScH under comparable conditions. The rates of H/D exchange for CH_4 and $Si(CH_3)_4$ are nearly the same, and the predominant exchange products at low conversion are CH_3D and $Si(CH_3)_n(CH_2D)_{4-n}$, indicating that there is one exchange per interaction with the metal complex. In contrast, $PtCl_4^{2-}$ [11] and zirconium alkoxides [12] show multiple exchanges per interaction with the metal complex for H/D exchange.

Intermolecular H/D exchange is also observed for several 2^o C-H bonds, but the rate for this exchange is generally very slow compared to inter- or intramolecular exchange of 1^o C-H bonds. Examples of slowly exchanging 2^o C-H bonds are found in $CH_3\underline{CH}_2CH_3$, the β-positions of THF, and cyclopentane. The rate of H/D exchange for cyclopentane was measured at 120°C and found to be 0.06 turnovers/hour (1.4 turnovers/day).[13] Two cases of readily exchangable 2^o C-H

groups are the α-positions of THF and cyclopropane. When cyclopropane is treated with Cp^*_2ScD in C_6D_6, H/D exchange occurs smoothly at a rate comparable to that observed for CH_4 or $Si(CH_3)_4$. Ring opening has not been observed.

A scale can be constructed that represents the relative ease with which Cp^*_2ScH will catalyze H/D exchange for a particular substrate, and is shown below: [14]

H_2 >> arenes >> Cp*, α-THF, $P(CH_3)_3$ > Cp*($Cp^*_2Sc(THF)H$) > CH_4, $Si(CH_3)_4$, C_3H_6(cyclopropane), $C_6H_6\underline{CH_3}$ > $\underline{CH_3}CH_2\underline{CH_3}$ >> β-THf, C_5H_{10}(cyclopentane), $CH_3\underline{CH_2}CH_3$.

Several trends can be seen in this scale. First, the fastest rates of exchange are observed for those R-H bonds with the most s character. This can be seen in the series H_2(s) >> aryl-H(sp^2) >> C-H(sp^3). This trend will be discussed in detail in following sections. Second, intramolecular H/D exchange is more facile than intermolecular exchange among C-H bonds with similar s character. This is expected since the intramolecular exchange should have a far lower entropy of activation than intermolecular exchange. Third, the steric bulk of the substrate is very important. The wedge that the hydride sits in is very restrictive, and 2^o carbons may not be able to fit into this wedge to react with the active site. Thus intermolecular H/D exchange at 2^o carbons would be expected to be slower than at 1^o ones.

The obvious exception is cyclopropane, which we feel is accelerated by the increased s character in its C-H bonds [15] (vide infra).

Thermochemistry of Scandiumhydride and -phenyl Complexes. In addition to catalyzing H/D exchange between H_2 and benzene, Cp^*_2ScH reacts reversibly with benzene to form $Cp^*_2ScC_6H_5$ and liberate H_2 (eq 7).

$$Cp^*_2ScH + C_6H_6 \rightleftharpoons Cp^*_2ScC_6H_5 + H_2(g) \qquad (7)$$

This equilibrium is evident if isolation of the hydride complex is attempted. When Cp^*_2ScH is generated in C_6H_6 solution and the solvent then removed slowly in vacuo, the product obtained is largely $Cp^*_2ScC_6H_5$. The equilibrium is driven to the right by removal of H_2 with the arene solvent. If H_2 is added back to the system, Cp^*_2ScH is reformed.

The experiment to measure the equilibrium constant for this reaction was initiated with Cp^*_2ScH in benzene solvent. We were unable to approach this equilibrium from the right side of equation 7 ($Cp^*_2ScC_6H_5 + H_2$) under our experimental conditions, because of the difficulty in accurately adding a very small amount of H_2 to an NMR sample. We are confident, however, that we are observing a true equilibrium, since a given sample may be cycled between 25°C and 80°C and give consistent values for the equilibrium constant at each tem-

perature.The equilibrium constants and ΔG^{o} values at several temperatures are given in Table 1.

Table 1. Equilibrium constants and ΔG^{o} values for the equilibrium between Cp^*_2ScH and $Cp^*_2ScC_6H_5$ in benzene solution (eq 7).

Temperature (^{o}C)	K_{eq} (x 10^6)	ΔG^{o}(kcal/mol)
6	2.8 ± 0.4	7.10 ± 0.8
25	5.6 ± 0.7	7.15 ± 0.9
47	13 ± 2	7.19 ± 0.10
66.5	23 ± 4	7.22 ± 0.13
80	36 ± 5	7.20 ± 0.13

From the temperature dependence of the equilibrium constant, we were able to determine ΔH^{o} and ΔS^{o} for this reaction. Plotting $\ln(K_{eq})$ *versus* $1/T$ gives a straight line with a slope equal to $-\Delta H^{o}/R$ and an intercept of $\Delta S^{o}/R$ (Figure 1), from which we calculated a ΔH^{o} of 6.7 ± 0.3 kcal/mol. From ΔG^{o} and ΔH^{o} we calculated a ΔS^{o} of -1.5 ± 0.1 e.u.. For similar C-H bond activation reactions it has been postulated that the free energy of equilibrium is equal to the enthalpy of equilibrium and that the entropy of equilibrium is negligible.[16] Our results support this postulate, since ΔG^{o} averages 7.2 kcal/mol for reaction 1,

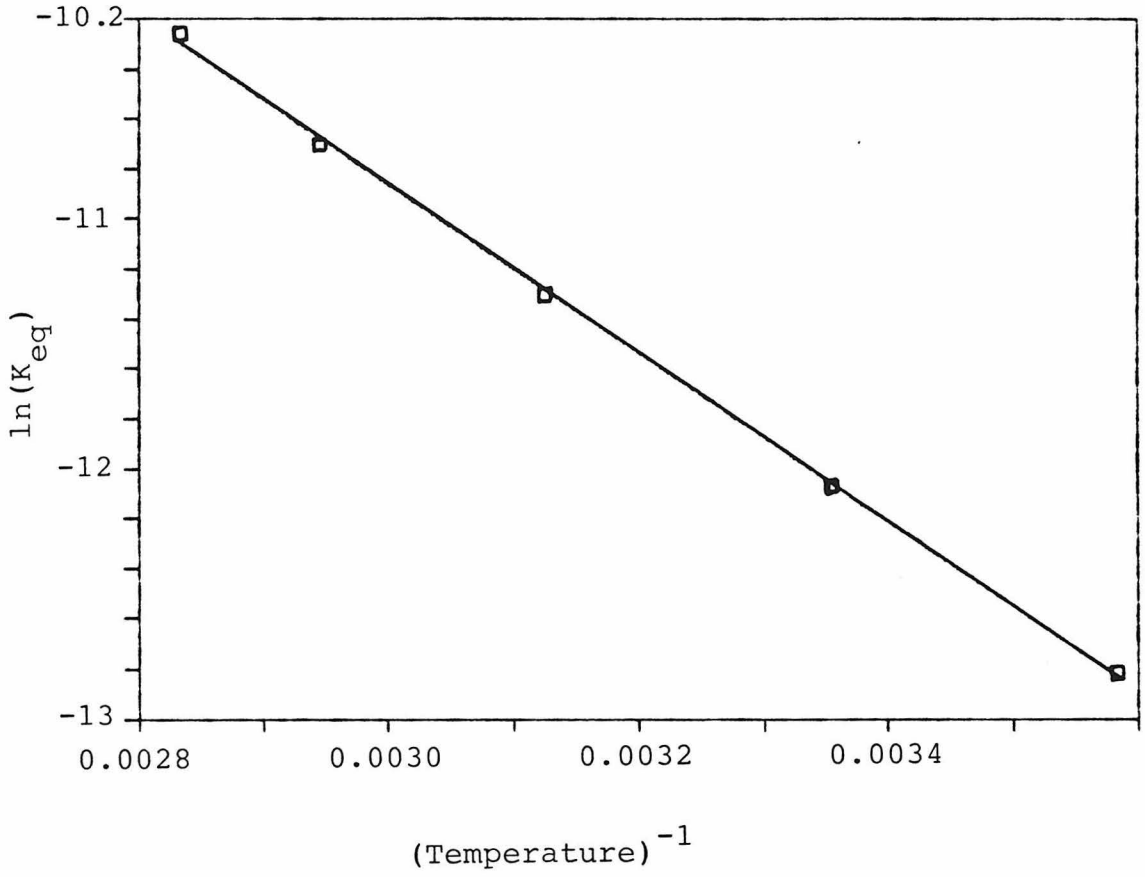


Figure 1. van't Hoff plot for the equilibrium between Cp^*_2ScH and $Cp^*_2ScC_6H_5$ in C_6H_6 solution.

with 6.7 kcal/mol of this being attributed to the enthalpy of the reaction. Using 110.9 kcal/mol for the C-H bond strength in benzene, [17] 104.2 kcal/mol for the H-H bond strength,[18] and 1.5 kcal/mole as the heat of solution of H_2 in benzene ($\Delta H_{soln} = H_{liq} - H_{gas}$) [19] we calculated from the enthalpy of the reaction that the scandium-hydride bond is 1.5 kcal/mole stronger than and the scandium-phenyl bond. Thermochemical measurements made by Marks, et al. ,[20] on a related thorium system ($Cp^*_2ThR_2$; R = hydride, phenyl) showed that a thorium-hydride bond is ca. 7 kcal/mol stronger than a thorium-phenyl bond.

$Cp^*_2Sc(THF)H$ is also in equilibrium with a scandium-phenyl complex (eq 8).

$$Cp^*_2Sc(THF)H + C_6H_6 \rightleftharpoons Cp^*_2ScH + THF + H_2(g) \quad (8)$$

The equilibrium constants and ΔG^o values for this reaction are given in Table 2. Plotting $\ln(K_{eq})$ versus $1/T$ again yields a straight line (Figure 2) and allows the calculation of 18.9 $\pm$ 0.8 kcal/mol for the enthalpy of this reaction. A value of 24.5 $\pm$ 2.0 e.u. is determined for ΔS^o from the ΔG^o and ΔH^o values. By comparison of reactions 7 and 8 it is expected that the reaction of $Cp^*_2Sc(THF)H$ should be the more endothermic, since both a scandium-hydride bond and a scandium-OC_4H_8 bond must be broken to form products.[21] It is also expected that the entropy for

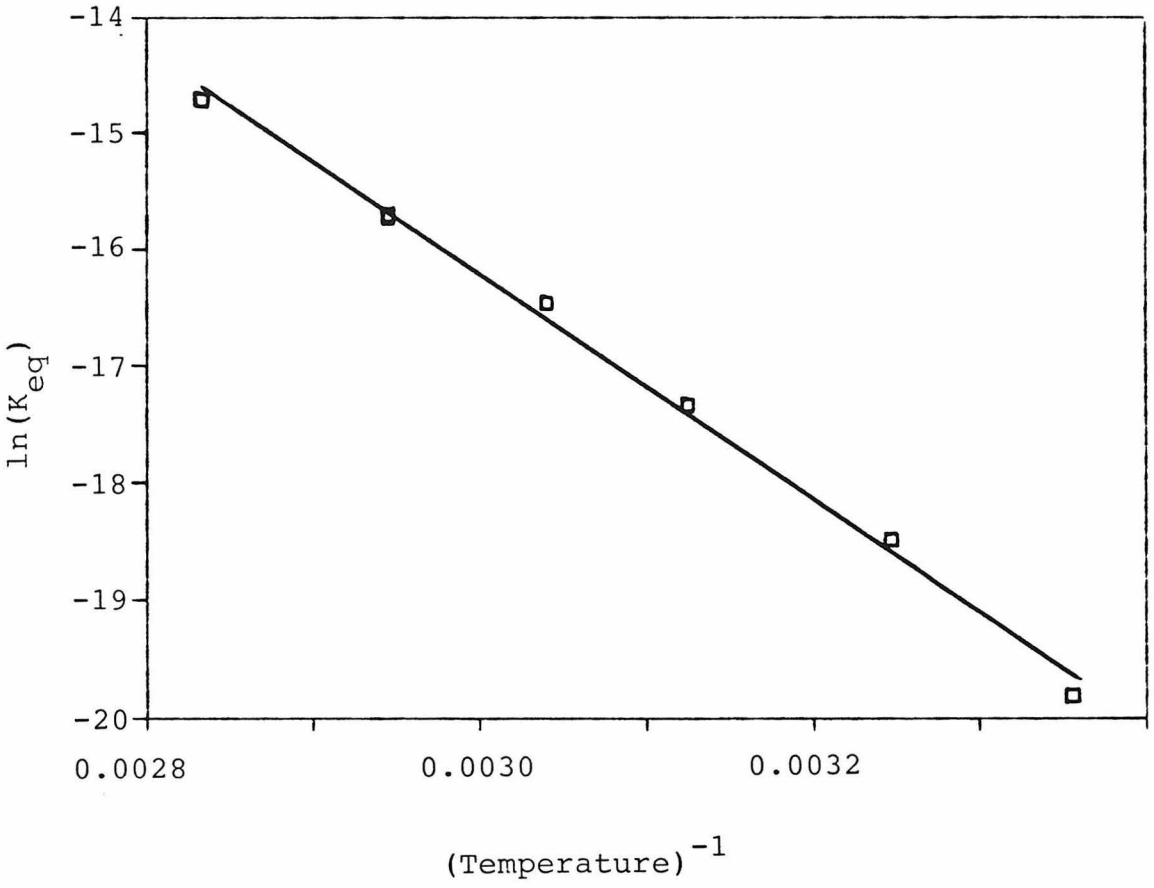


Figure 2. van't Hoff plot for the equilibrium between $Cp^*_2Sc(THF)H$ and $Cp^*_2ScC_6H_5$ in C_6H_6 solution.

reaction 8 should be large and positive, since two molecules are reacting to yield three molecules.

Table 2. Equilibrium constants and ΔG^{o} values for the equilibrium between $Cp^*_2Sc(THF)H$ and $Cp^*_2ScC_6H_5$ in benzene solution (eq 8).

Temperature (^{o}C)	K_{eq} (x 10^8)	ΔG^{o} (kcal/mol)
25	0.25 ± 0.03	11.7 ± 0.1
35	0.9 ± 0.1	11.3 ± 0.1
47	2.9 ± 0.4	11.0 ± 0.1
56	7.2 ± 0.9	10.8 ± 0.1
66.5	15 ± 2	10.6 ± 0.1
80	41 ± 6	10.3 ± 0.1

From these measurements, partial potential surfaces for reactions 7 and 8 can be constructed (Figure 3). This figure schematically shows that the predicted energy of the Sc-THF bond is 12 kcal/mol, assuming that the Sc-H bond strength is not changed on forming the THF adduct. This is a gross assumption, and the predicted bond strength of the Sc-THF bond should be treated as approximate. It must also be noted that the standard states for the equilibria of Cp^*_2ScH (eq 7) and $Cp^*_2Sc(THF)H$ (eq 8) with $Cp^*_2ScC_6H_5$ are

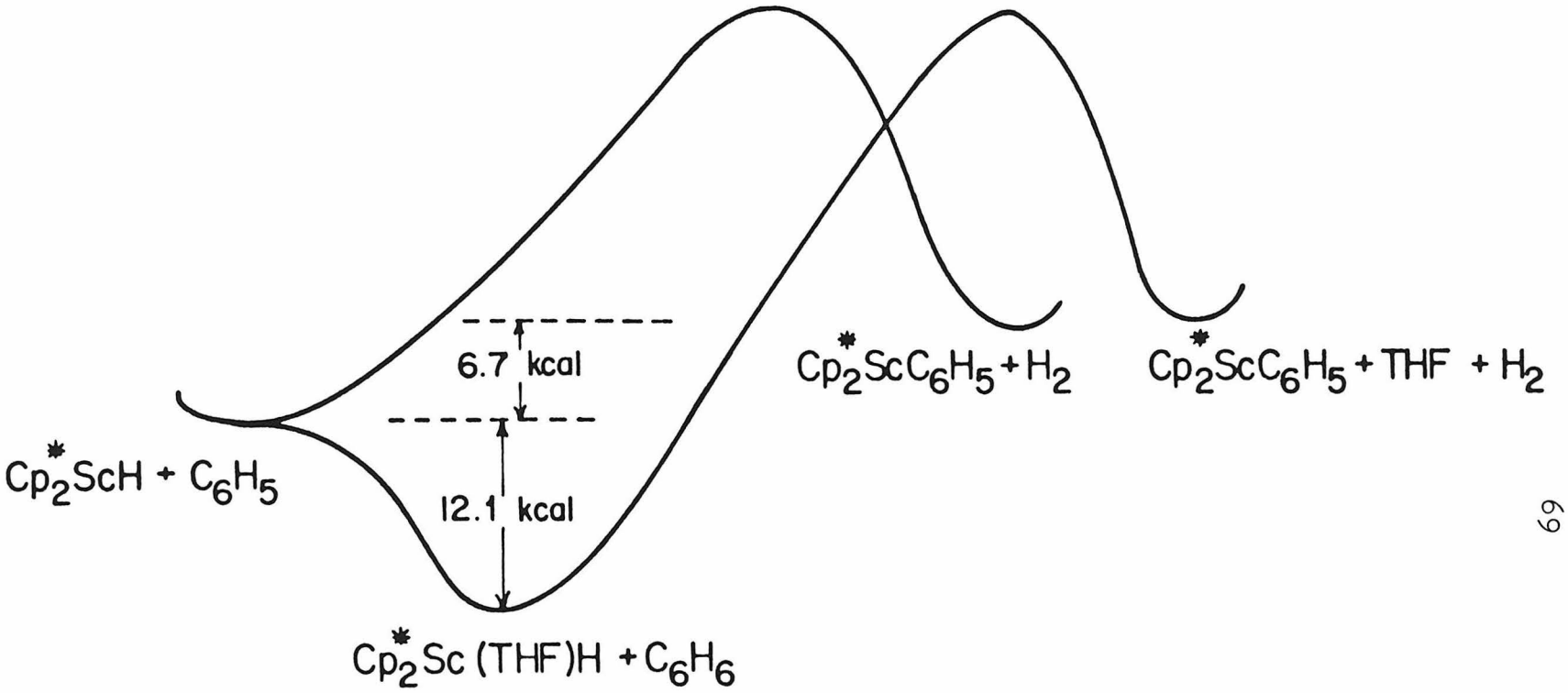


Figure 3. Partial potential surfaces for equilibria 7 and 8.

different. The latter equilibrium produces one mole of THF per mole of $Cp^*_2ScC_6H_5$, changing the properties of this solution relative to pure benzene. We expect this difference to be small.

We are attempting to extend this series to include equilibrations with an sp^3 carbon, but have not yet found a substrate that can compete with intramolecular C-H bond activation. An approximate upper limit can be placed on the strength of a scandium-carbon(sp^3) bond, however. When Cp^*_2Sc-n-butyl is dissolved in a 1:1 mixture of C_6H_6 and butane, $Cp^*_2ScC_6H_5$ is formed immediately and is the only scandium product visible in the NMR spectrum after ten minutes. When $Cp^*_2ScC_6H_5$ is dissolved in neat butane, the scandium-butyl complex is not formed, and prolonged heating leads only to intramolecular C-H activation, releasing C_6H_6. Assuming that there be as much as 3% scandium-butyl complex and it would not be observed in the NMR, and assuming that ΔS^o for the reaction is small, leads to a scandium-butyl bond strength that is at least 23 kcal/mol weaker than a scandium-phenyl (or scandium-hydride) bond. Metal-carbon and metal-hydride bond strength have been measured for a large number of Co(III) and Mn(I) coordinatively saturated complexes.[22] The differences in energy between the metal-hydride and metal-alkyl bonds are generally 35-40 kcal/mol. The differences that Marks sees in his thorium system are

smaller; a thorium-phenyl bond is 18 kcal/mole stronger than a thorium-butyl bond.[20]

Intramolecular C-H Activation by $Cp^*_2ScCH_3$. $Cp^*_2ScCH_3$ reacts with benzene to give $Cp^*_2ScC_6H_5$ and CH_4 (eq 9).

$$Cp^*_2ScCH_3 + C_6H_6 \longrightarrow Cp^*_2ScC_6H_5 + CH_4 \qquad (9)$$

If this reaction is carried out under pseudo first order conditions in scandium (C_6H_6 solvent) and monitored by ^1H NMR, no intermediates or products other than $Cp^*_2ScC_6H_5$ are observed. The reaction is first order in scandium (different initial concentrations of $Cp^*_2ScCH_3$ give identical rates). In order to determine the deuterium isotope effect for this reaction, $Cp^*_2ScCH_3$ was also treated with C_6D_6. Again the reaction appears first order in scandium, but in this case the first order plots ($\ln(c/c_0)$ vs. time) are not linear. Similar results are obtained plotting either disappearance of starting material or appearance of product. Examination of the products of the C_6D_6 reaction (eq 10) shows that more than one mechanism may be involved in this reaction.

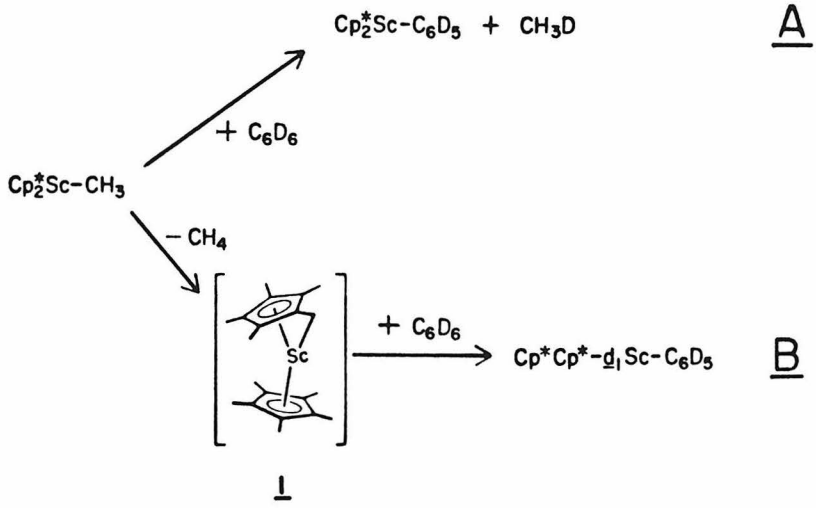
$$Cp^*_2ScCH_3 + C_6D_6 \xrightarrow{80^\circ C} Cp^*_2ScC_6D_5 + Cp^*Cp^*\text{-}\underline{d}_1ScC_6D_5 + CH_3D + CH_4 \qquad (10)$$

60% 40%

The direct bimolecular reaction of $Cp^*_2ScCH_3$ with C_6D_6 should produce only CH_3D,[23] rather than the 60:40 mixture

of $CH_3D:CH_4$ that is observed at 80°C. When the phenyl product of the C_6D_6 reaction is isolated and its ^2H NMR measured, peaks are observed for the phenyl ligand and a resonance assignable to a Cp* ligand of $Cp^*_2ScC_6D_5$.

The proposed mechanisms for the reaction of $Cp^*_2ScCH_3$ with C_6D_6 are shown in scheme 2.



Scheme 2

This scheme consists of two competing pathways. The first pathway, A, has a bimolecular rate determining step, which leads to direct intermolecular C-D activation, forming CH_3D. The second pathway, B, has a unimolecular rate determining step, involving intramolecular C-H activation to give a Cp* metallated intermediate, 1, and CH_4. 1 then reacts with C_6D_6 to give $Cp^*Cp^*\text{-}d_1ScC_6D_5$. Ring metallated complexes, similar to 1, are common in group IV permethylmetallocene

chemistry.[24] As the temperature of the reaction of $Cp^*_2ScCH_3$ with C_6D_6 is increased the ratio of CH_3D to CH_4 becomes richer in CH_4 (Table 3), implying that activation of Cp* C-H bonds becomes more prominent at higher temperatures.

TABLE 3. Ratio of CH_3D to CH_4 from the reaction of $Cp^*_2ScCH_3$ with C_6D_6 (eq 10).

TEMPERATURE	% CH_3D	% CH_4
60	76	24
80	60	40
98	53	47
125	50	50

In order to show that a tuck-in complex was a viable intermediate in this benzene reaction its synthesis and reactivity were investigated. When $Cp^*_2ScCH_3$ is heated in cyclohexane, CH_4 is released and a crystalline material, X, is produced.

$$Cp^*_2ScCH_3 \xrightarrow{80^oC} X + CH_4 \qquad (11)$$

We have been unable to determine the molecular weight of X, but an NMR spectrum can be obtained (Figure 4) that is consistent with one normal Cp* ($C_5(CH_3)_5$) and one metallated Cp* ligand ($\overline{Sc(\eta^5\text{-}C_5(CH_3)_4CH_2}$), thus we concluded that X was

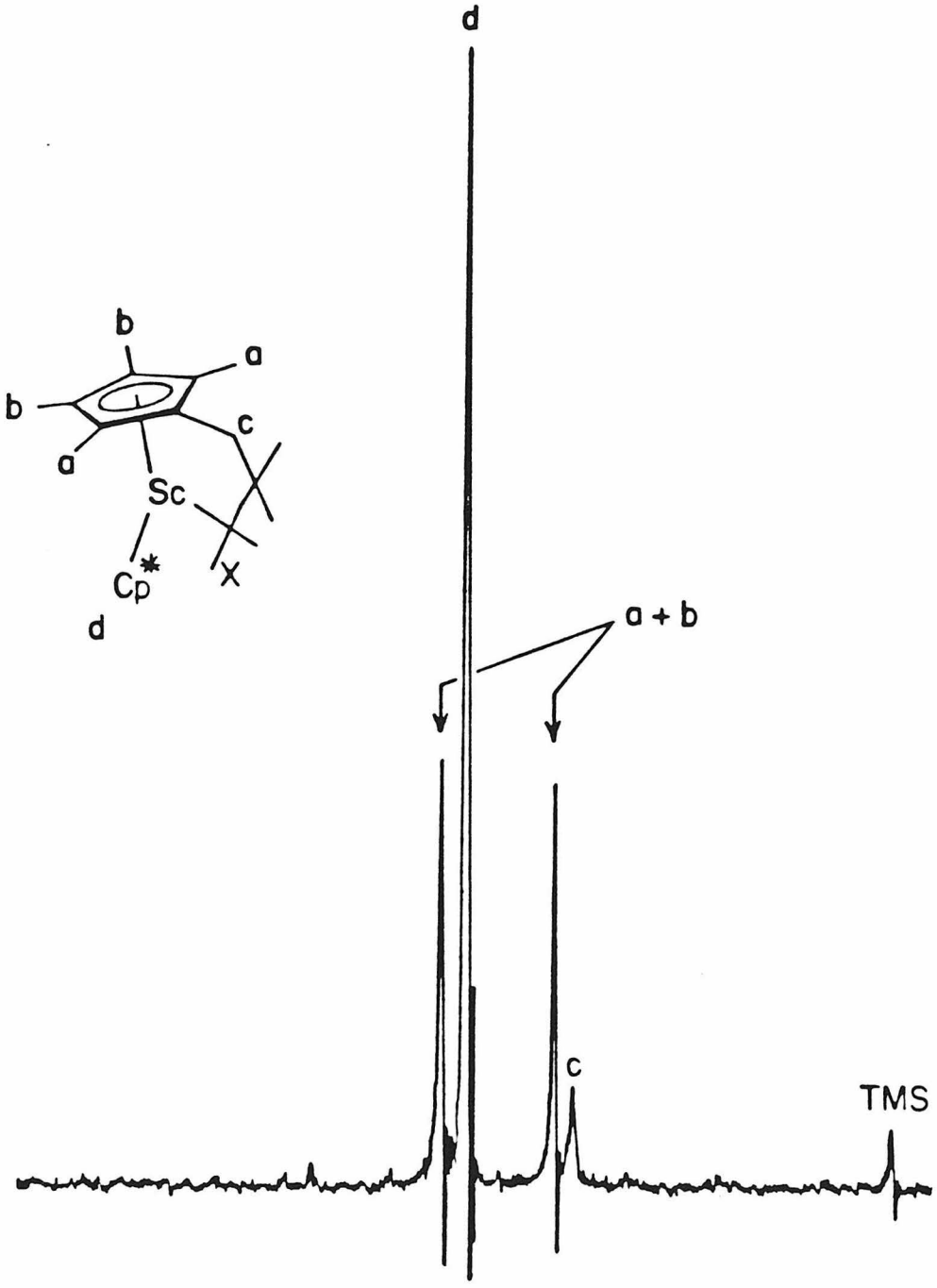


Figure 4. 90 MHz ^{1}H NMR spectrum of X.

an oligomeric tuck-in complex. Treatment of a benzene slurry of X with H_2 causes the solid to go into solution and forms exclusively Cp^*_2ScH (eq 12), which is common reactivity for ring metallated complexes.[25]

$$\underline{X} + H_2 \longrightarrow Cp^*_2ScH \qquad (12)$$

If X is pyrolyzed in C_6D_6, d_1-$Cp^*Cp^*ScC_6D_5$ is formed (identified by ^1H and ^2H NMR, eq 13), which is consistent with pathway B of Scheme 2.

$$\underline{X} + C_6D_6 \longrightarrow Cp^*Cp^*\text{-}\underline{d}_1ScC_6D_5 \qquad (13)$$

One piece of evidence argues strongly against X being a simple tuck-in complex. The number of moles of methane generated by reaction 11 (measured by Toepler pump) is only 80% of the number of moles of $Cp^*_2ScCH_3$ present at the start of the reaction. Thus, up to 20% of the scandium in X could still have a methyl ligand. A resonance directly assignable to this methyl ligand has not been observed. Using a higher field instrument (400 MHz) give a spectrum identical to that obtained with a 90 MHz spectrometer (Figure 5).

The tuck-in reaction (eq 11) shows the same kinetic behavior that was seen in the reactions of $Cp^*_2ScCH_3$ with benzene. The reaction is apparently first order (different initial concentrations of $Cp^*_2ScCH_3$ give the same initial rates) but the first order plots of the data are non-linear, see Figure 5. The initial rate of this reaction is (6.1 $\pm$

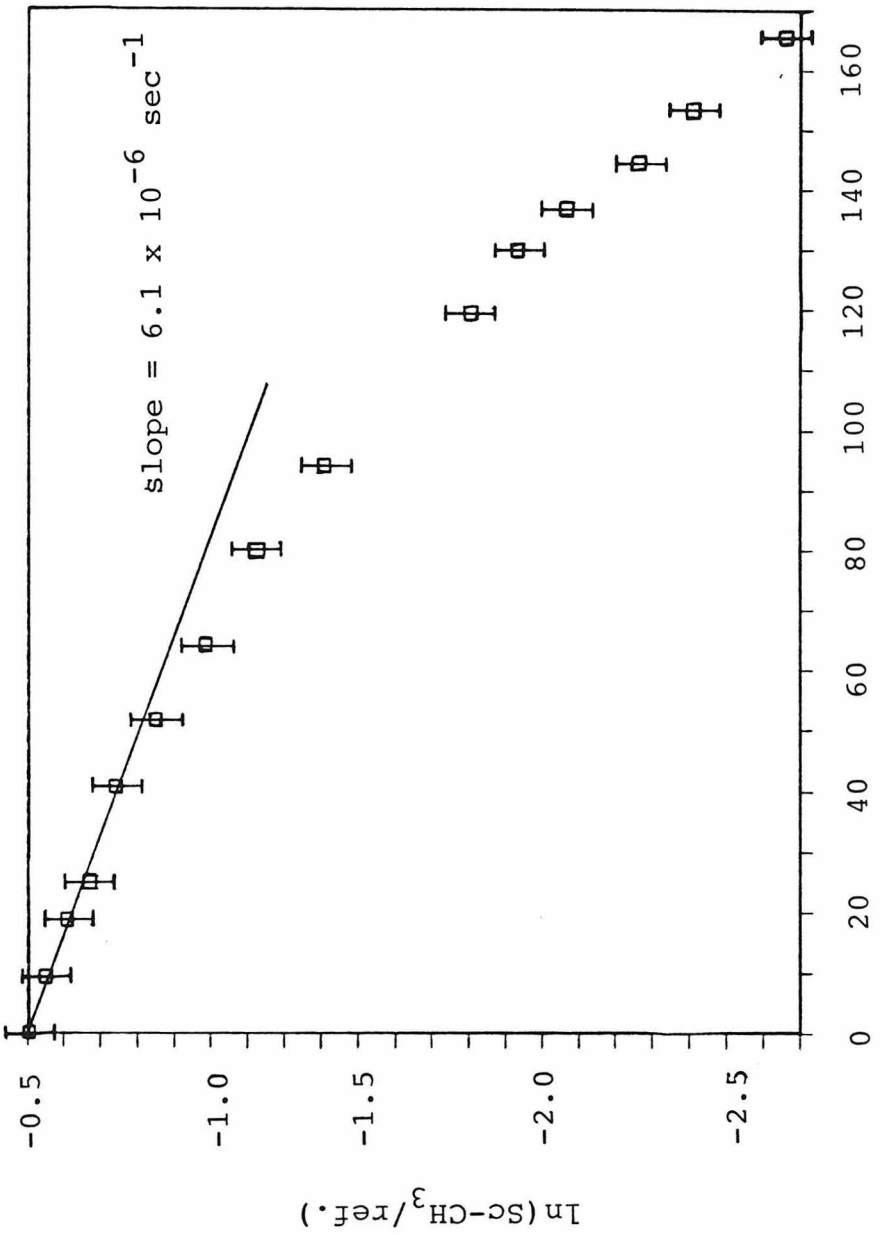


Figure 5. First order plot of the data from the reaction generating the "tuck-in" complex (eq 11).

0.8) x 10^{-6} sec^{-1} (based on *ca.* 75% of one half-life). The reaction mixture turns from yellow to red-brown after only short reaction times and remained this color throughout the course of the reaction. After approximately one half-life solid **X** begins precipitating and the rate of disappearance of $Cp^*_2ScCH_3$ increases by *ca.* a factor of two. This rate continues to increase with longer reaction times. If, in a separate experiment, $Cp^*_2ScCH_3$ is pyrolyzed in C_6D_{12} with solid **X** added at the beginning of the reaction, the first order plot is close to linear for over two half-lives, Figure 6, and the initial rate of this reaction is equal to the one observed shortly after **X** began precipitating in the previous experiment (without added **X**). This result strongly suggests that the decomposition of $Cp^*_2ScCH_3$ to give **X** is autocatalytic. $(Cp^*\text{-}\underline{d}_{15})_2ScCH_3$ was prepared and the kinetics of its thermal decomposition followed. This compound showed the same nonlinear kinetic behavior as the perprotio analogue, with an initial rate constant of (3.8 $\pm$ 0.4) x 10^{-6} sec^{-1}. A k_H/k_D of 1.6 is thus determined for the reaction of $Cp^*_2ScCH_3$ to give **X**

The decomposition of $Cp^*_2ScCH_3$ to give **X** is a mechanistic nightmare. The products of this reaction apparently catalyze their own formation. And in up to 20% of the reaction this catalysis may be incomplete, leaving some of the product with intact scandium-methyl bonds. To further complicate the situation, the rate of the reaction increases

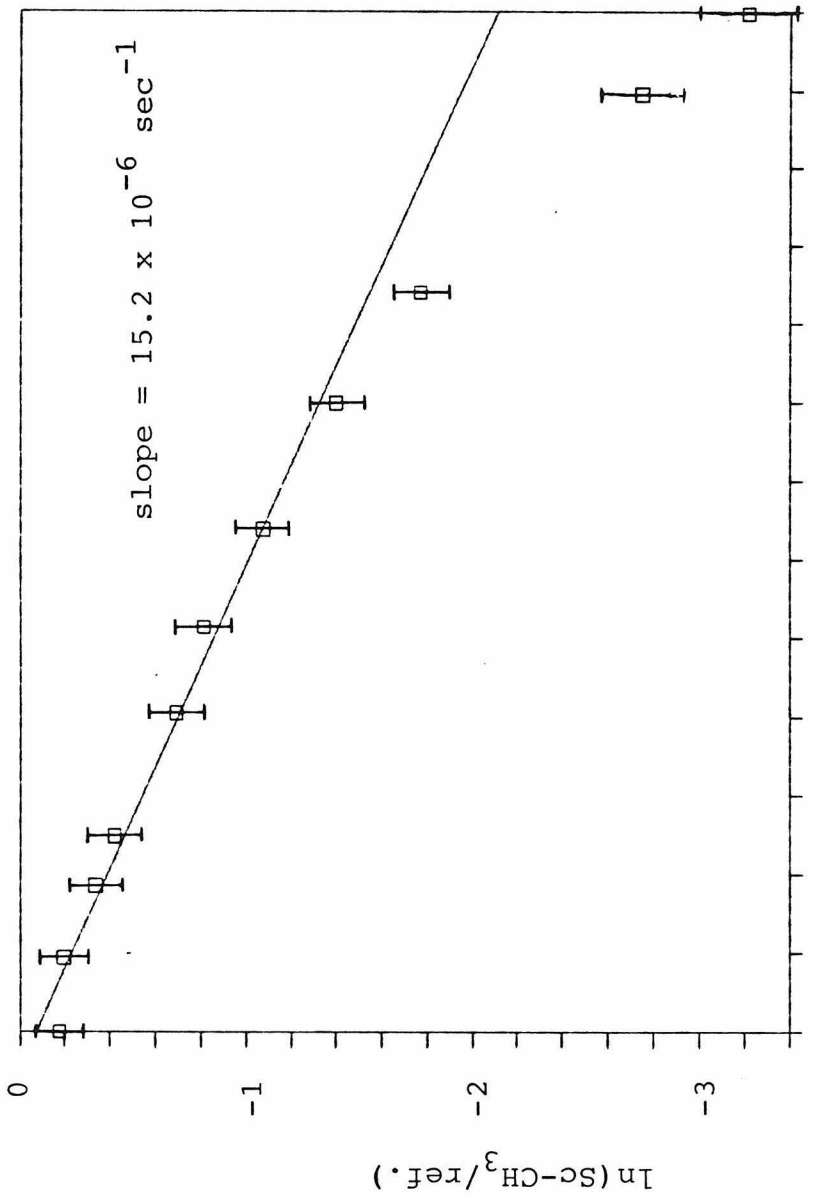


Figure 6. First order plot of the data from the reaction generating the "tuck-in" complex, with added **X**.

rapidly after X begins to precipitate, so heterogeneous reactions may also be occurring. The disappearance of $Cp^*_2ScCH_3$ in this reaction is a function of several processes. Thus, the observed deuterium isotope effect is a composite of several deuterium isotope effects, and probably does not reflect directly on an intramolecular C-H bond breaking process. Rather than investigate the mechanism of the tuck-in reaction deeply, we chose to just examine its characteristics, so that Cp* C-H activation can be excluded as a mechanistic pathway in other reactions. The most obvious characteristic of this reaction is the label exchange. When $Cp^*_2ScCH_3$ is reacted with C_6D_6, significant amounts of CH_4 are formed, indicating that activation of Cp* C-H bonds has occurred. The converse labeling experiment can also be carried out. If $(Cp^*\text{-}\underline{d}_{15})_2ScCH_3$ is treated with a substrate bearing only C-H bonds (as opposed to C-D bonds), and only CH_4 is observed, then intramolecular C-D activation is not occurring. The initial rate of the tuck-in reaction (eq 11) is $(6.1 \pm 1.0) \times 10^{-6}$ sec^{-1}, so if a particular reaction has a rate significantly faster than this, then the reaction is most likely not going through activation of a Cp* C-H bond. Lastly, if the activation of Cp* C-H bonds is a significant mechanistic pathway for a reaction involving $Cp^*_2ScCH_3$, the first order kinetic plots will be decidedly curved, with the rate increasing for longer reaction times.

The unimolecular mechanism proposed for the reaction of $Cp^*_2ScCH_3$ with C_6D_6 is obviously over-simplified. The proposal that only 1 reacts with C_6D_6 to give Cp^*Cp^*-$\underline{d}_1ScC_6D_5$ may be wrong, since several similar species may be present. The proposal that CH_4 is eliminated to give a tuck-in complex is still valid, but the structure of this complex is unknown. To determine the isotope effect for an intermolecular C-H activation reaction by $Cp^*_2ScCH_3$ the direct bimolecular reaction of $Cp^*_2ScCH_3$ with benzene (A of Scheme 2) was examined. In order to minimize the amount of the reaction that would go by the tuck-in route, $(Cp^*\text{-}\underline{d}_{15})_2ScCH_3$ was used. Linear first order kinetics are observed for the reactions of d_{30}-$Cp^*_2ScCH_3$ with both C_6H_6 and C_6D_6 solvents, giving initial pseudo first order rates of $(1.4 \pm 0.05) \times 10^{-4}$ and $(5.1 \pm 0.1) \times 10^{-5}$ sec^{-1}, respectively. The rate of the tuck-in reaction was 3% and 8% of the observed rate constants for the C_6H_6 and C_6D_6 reactions, respectively. The rate of the tuck-in reaction was subtracted from each of the two rate constants to give the two corrected rate constants, whose ratio is 2.9 ± 0.4 $(k_{C_6H_6}/k_{C_6D_6})$.

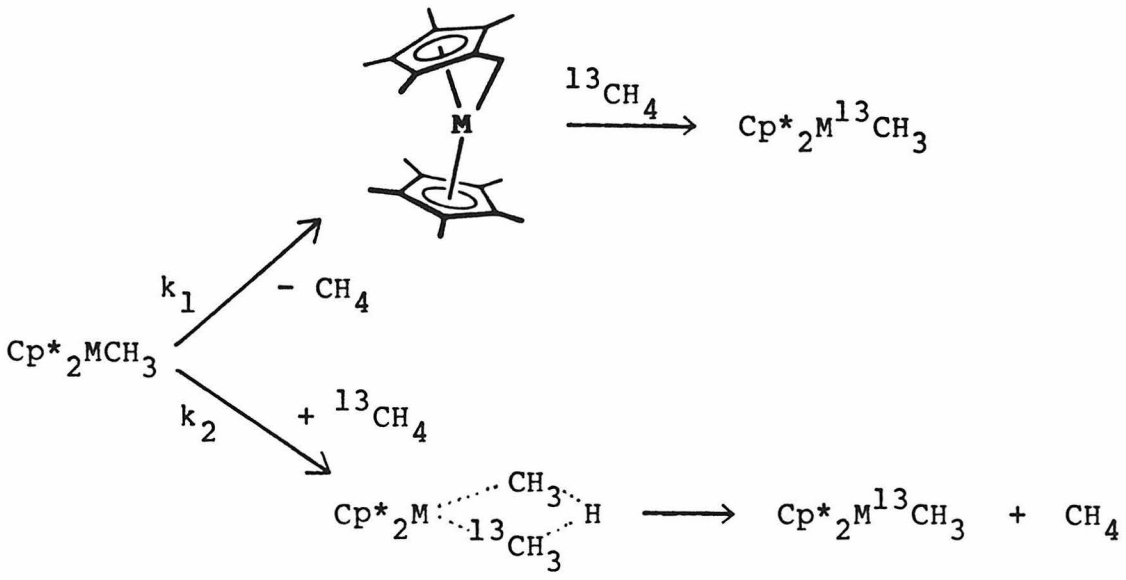
C-H Activation by Scandiumalkyl and -aryl Complexes. Methane is the simplest of all hydrocarbons, but has been the most difficult to activate. The first activation of methane by an inorganic complex was demonstrated by Shilov 16 years ago.[26] He found H/D exchange between

D_2O/CH_3CH_2OOD and CH_4 is catalyzed by K_2PtCl_4. Only recently has activation of methane, which led to an isolated metal-methyl complex, been reported. A few group VIII complexes have been found to react with methane to yield methylhydride complexes,[1(f), 27] while examples of lanthanide and actinide complexes, which give methyl complexes, have been communicated.[28] $Cp^*_2ScCH_3$ activates methane as shown in equation 14.

$$Cp^*_2ScCH_3 + {}^{13}CH_4 \xrightarrow[C_6D_{12}]{70^oC} Cp^*_2Sc{}^{13}CH_3 + CH_4 \qquad (14)$$

This reaction was done with a large excess of the labeled methane ($[{}^{13}CH_4]$ = 0.5-1.5 M; $[Cp^*_2ScCH_3]$ = 0.06 M). A second order rate constant of 1 x 10^{-5} $M^{-1}sec^{-1}$ was obtained.

Watson has measured the rate of this reaction for complexes isoelectronic with $Cp^*_2ScCH_3$, $Cp^*_2MCH_3$ (M = Y, Lu).[28(a)] She found the yttrium complex reacted five times faster than the lutetium one, while the scandium compound reacts fifty times slower than the lutetium compound (k_Y = 2.6 x 10^{-3} $M^{-1}sec^{-1}$; k_{Lu} = 4.6 x 10^{-4} $M^{-1}sec^{-1}$). She proposes a two part mechanism for this reaction, shown in Scheme 3.[29] One pathway of this methane activation reaction involves the direct bimolecular reaction of $Cp^*_2MCH_3$ with ${}^{13}CH_4$, while the second involves a unimolecular reaction of $Cp^*_2MCH_3$ to give a tuck-in complex, followed by its reaction with ${}^{13}CH_4$ to give $Cp^*_2M{}^{13}CH_3$.



Scheme 3

For the lutetium complex the uni- and bimolecular rate constants were reported (k_1 = 2.3 x 10^{-5} sec^{-1}, k_2 = 4.7 x 10^{-3} $M^{-1}sec^{-1}$). Yttrium and lutetium have the same ionic radius (Y(III) = Lu(III) = 0.93 Å), so steric interactions should be the same for both metals and any differences in their reactivity attributable to electronic differences in the metals. Watson ascribes the greater reactivity of yttrium over lutetium to yttrium's greater electrophilicity. Scandium can not be directly compared to Y or Lu. It is very electrophilic, but its ionic radius (Sc(III) = 0.81 Å) is much smaller than that of Y or Lu, which acts to amplify any unfavorable steric interactions. It is interesting that both the uni- and bimolecular pathways for the reaction of $Cp^*_2LuCH_3$ with methane are faster than the total reaction of $Cp^*_2ScCH_3$ with methane, suggesting that steric interactions

decrease the rate of both the uni- and bimolecular reactions.

$Cp^*_2ScCH_3$ reacts with styrene and substituted styrenes by activation of one of the terminal vinylic C-H bonds, forming a scandium styrenyl complex (eq 15).

$$Cp^*_2ScCH_3 + H_2C{=}CHC_6H_4X \longrightarrow Cp^*_2ScCH{=}CHC_6H_4X\text{-}\underline{t} + CH_4 \quad (15)$$

$$X = H,\ CH_3,\ OCH_3,\ CF_3$$

The stereochemistry of the product is assigned <u>trans</u> based on the large coupling constant observed for the two vinylic protons (i.e. $^3J_{H-H}$ = 20 Hz for $Cp^*_2ScC\underline{H}{=}C\underline{H}C_6H_4OCH_3$).[30] The kinetics of reaction 19 with X = OCH_3 and CF_3 were examined; both reactions are first order in scandium and styrene, and no intermediates are observed during the course of the reaction. The reactions were run with 2-4 times more styrene than scandium, and the data plotted using a standard second order equation [31] (eg. Figure 7), such that the observed rate constants are true second order rate constants. The rates of these reactions were measured at several temperatures, and activation parameters calculated for each reaction (using Arrhenius and activated complex theory). The Arrhenius plots for these reactions are shown in Figure 8, and the rate constants and activation parameters given in Table 4.

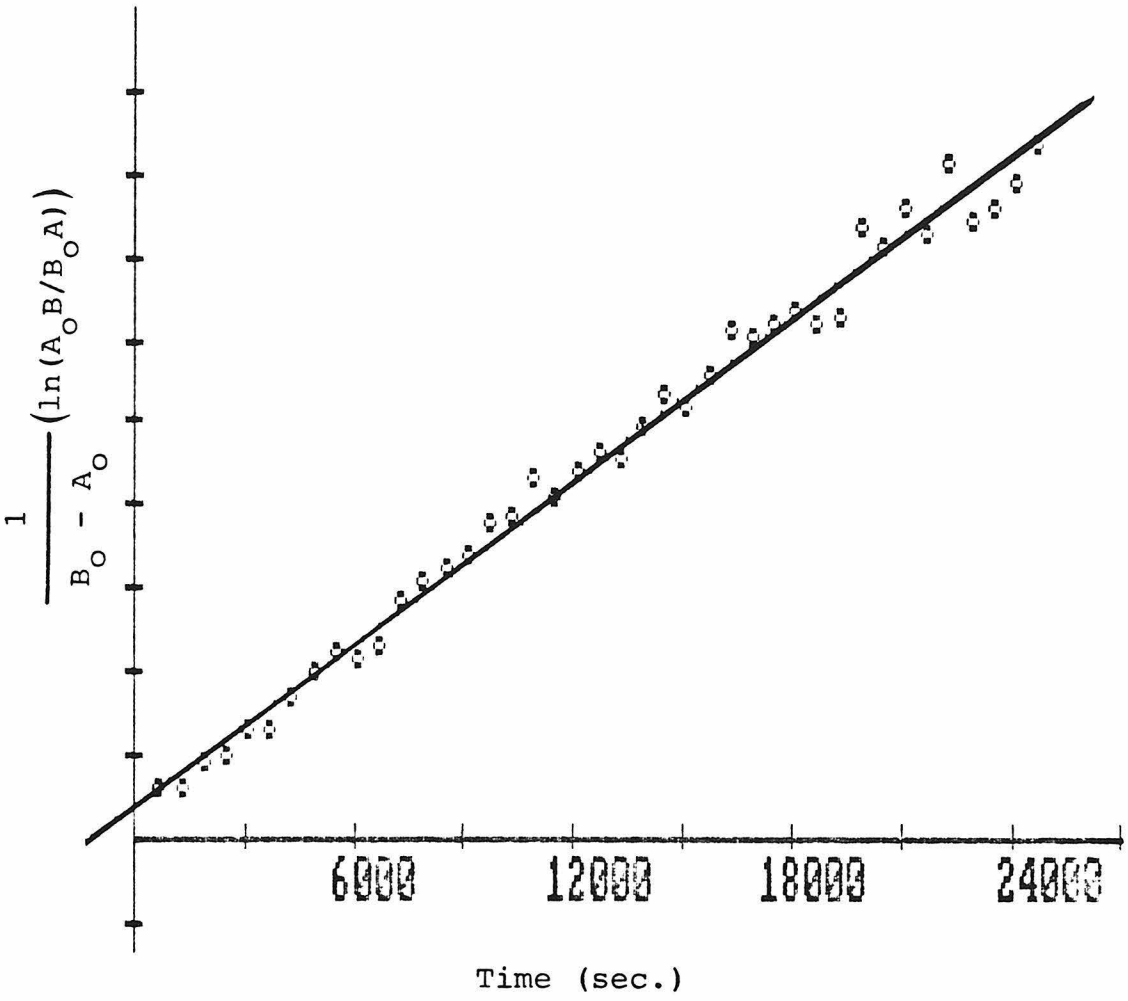


Figure 7. Representative second order plot for the reaction of $Cp^*_2ScCH_3$ with $H_2C{=}CHC_6H_4CF_3$-p. where A = $[Cp^*_2ScCH_3]$ and B = $[H_2C{=}CHC_6H_4CF_3]$.[31]

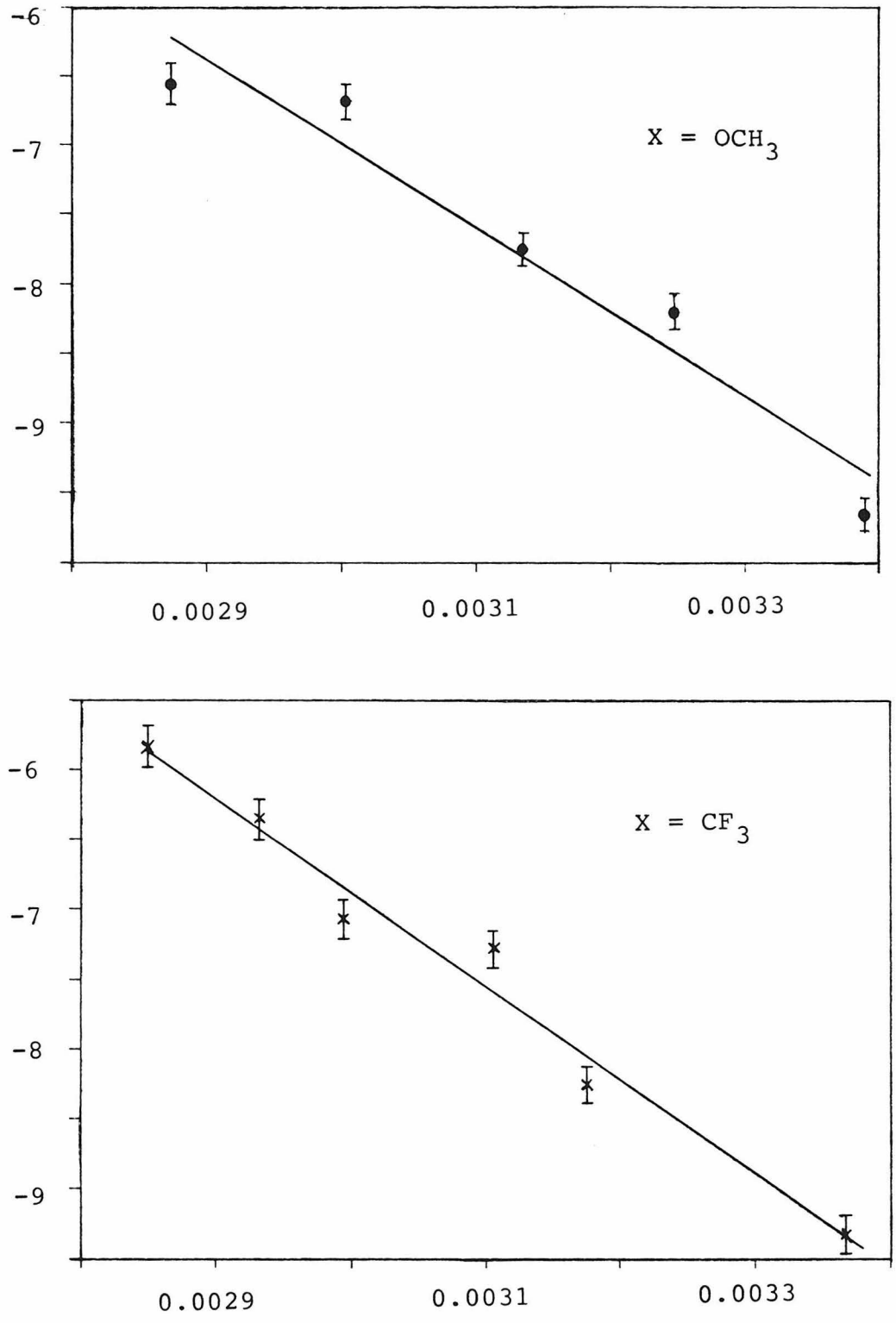


Figure 8. Arrhenius plots (ln(k) vs. 1/T) for the reactions of $Cp^*_2ScCH_3$ with $H_2C{=}CHC_6H_4X$-p (X = OCH_3, CF_3).

Table 4. Rate constants and activation parameters for the reaction of $Cp^*_2ScCH_3$ with substituted styrenes ($H_2C=CHC_6H_4X$-para; X = OCH_3, CF_3) at 60°C (eq 19).

X	OCH_3	CF_3
k_2 ($M^{-1}sec^{-1}$, x 10^4)	12.5 ± 0.7	8.5 ±0.5
E_a (kcal/mole)	12.1 ± 0.3	13.2 ±0.3
log A	4.9 ± 0.2	5.7 ± 0.2
$\Delta H^{\ddagger}$ (kcal/mol)	11.5 ±0.3	12.6 ± 0.3
$\Delta S^{\ddagger}$ (e.u.)	-38 ± 3	-34 ± 3

These reactions are typified by small enthalpies of activation and large negative entropies of activation, which is very characteristic of associative reactions with highly ordered transition states.[32] Large entropies of activation (-9 to -19 e.u.) are also observed for intramolecular C-H activation by d^0 complexes.[4, 5] Only small substituent effects on the rate of the reaction were observed (CF_3 and OCH_3 substituted styrenes gave very similar activation parameters). Rather than forming styrenyl complexes, Cp^*_2ScH reacts with styrene by insertion of the olefinic group into the Sc-H bond to give a phenethyl complex (eq 16).

$$Cp^*_2ScH + H_2C=CHC_6H_5 \longrightarrow Cp^*_2ScCH_2CH_2C_6H_5 \qquad (16)$$

$Cp^*_2ScCH_2CH(CH_3)_2$ reacts with propene to give only $Cp^*_2ScCH{=}CHCH_3$-t (eq 17).

$$Cp^*_2ScCH_2CH(CH_3)_2 \xrightarrow[CH_2=CHCH_3]{} Cp^*_2ScCH{=}CHCH_3\text{-t} + CH(CH_3)_3 \quad (17)$$

The η^3-allyl complex, $Cp^*_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$, is stable (vide supra), but is never formed in this reaction. The details of this reaction will be discussed in the following chapter.

$Cp^*_2ScCH_3$ reacts very rapidly with the alkynyl C-H bond of propyne to liberate methane and form a scandium propynyl complex (eq 18).

$$Cp^*_2ScCH_3 + HC{\equiv}CCH_3 \longrightarrow Cp^*_2ScC{\equiv}CCH_3 + CH_4 \quad (18)$$

Although the kinetics of this reaction were not investigated (due to complicating subsequent reactions, vide infra), the reaction is complete in minutes at temperatures below 0^oC. It is interesting to note that the product of alkyne insertion into the Sc-CH_3 bond ($Cp^*_2ScCH{=}C(CH_3)_2$) is not observed, even though the isobutenyl compound is stable and internal alkynes readily insert into scandium-methyl bonds (vide infra). Cp^*_2ScH also reacts with one equivalent of propyne to give only $Cp^*_2ScC{\equiv}CCH_3$ (eq 19).

$$Cp^*_2ScH + HC{\equiv}CCH_3 \longrightarrow Cp^*_2ScC{\equiv}CCH_3 + H_2 \quad (19)$$

Again, the inserted product ($Cp^*_2ScCH{=}CHCH_3$) is stable, but never observed. For analogous zirconium and hafnium hydride

complexes, rapid insertion of propyne into the M-H bonds is observed, leading to M-CH=CHCH$_3$-*t* complexes.[33]

Cp*$_2$ScR (R = methyl, aryl) react cleanly with arenes to give a scandium aryl complex and R-H (eq 20).

$$Cp^*_2ScR + H\text{-}C_6H_4X \longrightarrow Cp^*_2ScC_6H_4X + R\text{-}H \qquad (20)$$
$$R = \text{methyl, aryl; } X = H, \text{ alkyl, amide}$$

For reactions of a given arene, Cp*$_2$ScCH$_3$ always reacts more rapidly than Cp*$_2$ScC$_6$H$_5$. This is presumably due to increased steric crowding of the reactive site by the phenyl ligand compared to CH$_3$.

The reactions of Cp*$_2$ScCH$_3$ with arenes were studied extensively in order to probe the importance of coordination of the cloud in these C-H bond activating reactions. In the first experiments we examined the rates of activation of C-H bonds in monosubstituted arenes as a function of the substituent (eq 21).

$$(Cp^*\text{-}\underline{d}_{15})_2ScCH_3 + C_6H_5X \longrightarrow (Cp^*\text{-}\underline{d}_{15})_2ScC_6H_4X + CH_4 \qquad (21)$$
$$X = N(CH_3)_2, CH_3, H, CF_3$$

Since we were interested in the direct interaction of Sc-CH$_3$ with the aryl C-H bond, we used (Cp*-*d*$_{15}$)$_2$ScCH$_3$ to minimize the rate of the tuck-in pathway (*B* of Scheme 2). The tuck-in pathway would not be effected by substituents on the arene, because its rate determining step is activation of a

C-H bond of its own Cp* rings. In all cases the first order plots of these reaction are linear (eg. Figure 9) and the amount of CH_3D (formed by the tuck-in pathway) is 5% or less of the total methanes produced. Under the reaction conditions used, substrates with non-aryl protons ($C_6H_5N(CH_3)_2$ and $C_6H_5CH_3$) or fluorides ($C_6H_5CF_3$) yield only aryl scandium products. $Cp^*_2Sc-C_6H_4CF_3$ does react with additional $C_6H_5CF_3$ after prolonged heating, but the products of this reaction are not observed until well after reaction 25 is complete. The rate constants for these reactions at 80°C are given in Table 5.

Table 5. Rate constants for the reaction of $(Cp^*-d_{15})_2ScCH_3$ with C_6H_6 and substituted arenes (eq 24) at 80°C.[a]

arene	k_2 ($M^{-1}sec^{-1}$, x 10^5)
$C_6H_5N(CH_3)_2$	3.2 ± 0.1
$C_6H_5CH_3$	3.4 ± 0.1
C_6H_6	3.3 ± 0.1
$C_6H_5CF_3$	1.4 ± 0.1

[a] These reactions were carried out in C_6D_{12} solutions at 80°C; $[(Cp^*-d_{15})_2ScCH_3]$ = 0.12 M, [arene] = 1.3 M.

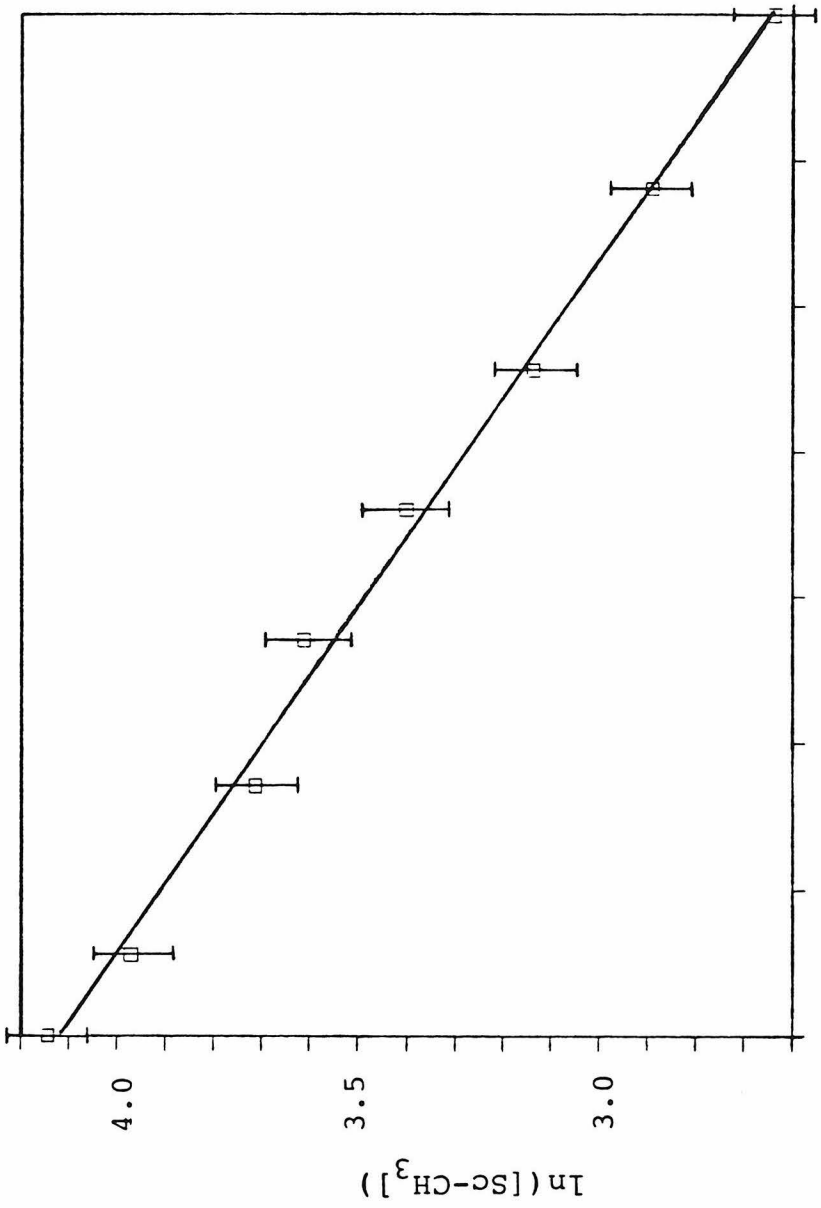


Figure 9. Representative first order plot of the data from the reaction of $Cp^*_2ScCH_3$ with $C_6H_5N(CH_3)_2$.

The rate of the reaction is reduced by a factor of two when the substituent on the arene is changed from strongly electron donating ($N(CH_3)_2$) to electron withdrawing (CF_3).

The positional preference for activation of the C-H bonds of toluene by $Cp^*_2ScCH_3$ was examined. The different tolyl isomers (ortho, meta, para) and the benzyl complex are all easily differentiated by 500 MHz NMR. The kinetic and thermodynamic product ratios for the reaction of Cp^*_2ScR (R = CH_3, $CH_2C_6H_5$ and $C_6H_4CH_3$) with toluene solvent are given in Table 6. The first three entries of Table 6 represent the kinetic ratios for the reactions of $Cp^*_2ScCH_3$ and $Cp^*_2ScCH_2C_6H_5$ with toluene, since authentic samples of $Cp^*_2Sc\text{-}C_6H_4CH_3$-o and $Cp^*_2Sc\text{-}C_6H_4CH_3$-p do not isomerize on the time scale of these lower temperature experiments (80°C). The kinetic and thermodynamic ratios of tolyl isomers are the same, since heating the ortho tolyl derivative eventually gives an unchanging ratio (entry 7 of Table 6) that is the same as the kinetic ratio. $Cp^*_2ScCH_2C_6H_5$ is one of the products formed in the reaction of $Cp^*_2ScCH_3$ with toluene. The percentages of benzylic product in the reactions of $Cp^*_2ScCH_3$ with toluene are definitely low, since $Cp^*_2ScCH_2C_6H_5$ reacts with solvent to give tolyl products at 80°C (entry 3 of Table 6). Both the kinetic and thermodynamic ratios have a predominance of meta and para tolyl isomers. The amount of meta isomer is always twice that of the para isomer, which coincides with the

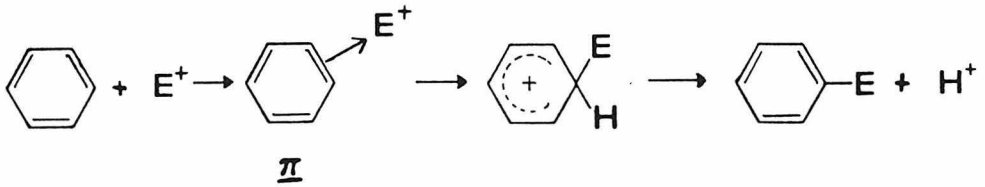
Table 6. Isomer ratios for the product mixtures from the reactions of $Cp^*_2ScCH_3$, $Cp^*_2ScCH_2C_6H_5$ and $Cp^*_2Sc\text{-}C_6H_4CH_3$-*o*, -*p* with toluene.

Reactant and conditions[a]	product ratios (relative %)[b]			
	ortho	meta	para	benzyl
$Cp^*_2ScCH_3$, 80°C, 2 hrs[c]	6(7)	57(66)	23(27)	14
$Cp^*_2ScCH_3$, 80°C, 7.5 hrs[d]	9(11)	52(62)	23(27)	16
$Cp^*_2ScCH_2C_6H_5$, 80°C, 7.5 hrs	3(5)	44(72)	14(23)	39
$Cp^*_2ScC_6H_4CH_3$-*o*, 80°C, 7.5 hrs	>95			0
$Cp^*_2ScC_6H_4CH_3$-*p*, 80°C, 7.5 hrs			>95	0
$Cp^*_2ScCH_3$, 115°C, 12 hrs	13	61	26	0
$Cp^*_2ScC_6H_4CH_3$-*o*, 115°C, 36 hrs	15	60	25	0

[a] All of these reactions were carried out in sealed tubes in toluene solvent, the given scandium complex was ca. 0.10 M. [b] The relative percentages were determined by cutting and weighing the NMR spectra of the tolyl-methyl and benzylic resonances. The numbers are accurate to ± 2%. Numbers in parentheses represent the relative % of each tolyl isomer when scandium benzyl is formed.
[c] Reaction *ca.* 40% complete. [d] Reaction *ca.* 75 % complete.

statistical ratio of these positions, indicating that the rates of reaction at the two positions are equal ($(2k_{para})/k_{meta} = 1$). The ortho tolyl isomer is presumably less stable for steric reasons.[34]

Scandium, being very Lewis acidic, is a fairly strong electrophile. For this reason we thought that the reactions of Cp^*_2ScR complexes with arenes may bear a resemblance to electrophilic aromatic substitution reactions, which have been studied extensively by physical organic chemists.[35] These reactions involve attack of an organic or inorganic electrophile on the arene π cloud, followed by σ-π rearrangement to give a Whelland type intermediate, which releases H^+ to give the substituted arene (Scheme 4).[36]



Scheme 4

Electrophilic aromatic substitution has also been studied with organometallic electrophiles. These electrophiles are generally cationic,[37] but anionic ones have also been claimed.[38] The mechanisms of substitution reactions of organometallic electrophiles on arenes are believed to be very similar to those proposed for organic and inorganic ones. The electrophile π-complex ($\underline{\pi}$) has actually been observed in the reaction of $Cp^*Re(NO)(CO)^+$ with arenes.[39]

Characteristic reactivity patterns are exhibited by most electrophiles in these substitution reactions, whether the electrophile is organic, inorganic, or organometallic.

In nearly every case the reactivity of Cp^*_2ScR with arenes is very different from any of these electrophiles. For example, in electrophilic aromatic substitution reactions, electron donating groups attached to the arene accelerate the rate of substitution, by stabilizing the positive charge on the arene; conversely, electron withdrawing groups act to slow this rate. For organic and inorganic electrophiles the rate difference between $C_6H_5N(CH_3)_2$ and $C_6H_5CF_3$ is generally 10^8-10^{10},[40] while for organometallic electrophiles this difference is 10^3-10^6.[38(b), 41] Scandium's rate difference of 2 is very small. Moreover, benzene and toluene react more rapidly than $C_6H_5N(CH_3)_2$, suggesting that electron donation or withdrawal by substituents does not affect the energy of the transition state.

Although large substituent effects on the rates of substitution are characteristic of electrophilic attack, they are not diagnostic. Very active electrophiles show small substituent effects, often reacting with toluene and benzene at nearly the same rate.[42] A more diagnostic characteristic of electrophilic attack is the positional selectivity for substitution on toluene. All electrophiles (even the

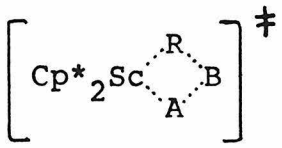
very active ones) show a high preference for substitution at positions ortho and para to the methyl group.[37(a)] The meta isomer accounts for <5% of the substitution products. This effect is a result of the methyl group adding stability to the intermediates or transition states with positive charge localized at positions para and ortho to it. For example, $Cp^*Re(NO)(CO)^+$ and H_2PtCl_6 ($PtCl_5^-$ is believed to be the active electrophile) react with toluene to give tolyl complexes; in both cases the major product results from para substitution ($(2k_{para})/k_{meta}$ = 32 and 18, respectively), with the ortho isomer not being observed. Substitution at the benzylic carbon is never observed. All of the scandium complexes investigated (Cp^*_2ScR; R = methyl, benzyl and tolyl) give tolyl products on treatment with toluene. These tolyl products have statistical distribution between meta and para substitution ($(2k_{para})/k_{meta}$ = 1), and low , but observable, substitution ortho to the methyl group. Moreover, $Cp^*_2ScCH_3$ gives large amounts (>15%) of the benzylic substitution product ($Cp^*_2ScCH_2C_6H_5$) on treatment with toluene. These results, and the observation that the rate of substitution is not strongly effected by electron donating or withdrawing groups, suggest that interaction of sc with the system of the arene is not important in the C-H activation of aryl C-H bonds by $Cp^*_2ScCH_3$.

Deuterium isotope effects are generally not observed in the reactions of organic and inorganic electrophiles with

arenes,[43] but an isotope effect of 3.0 was measured for the reaction of H_2PtCl_6 with benzene.[39] The authors do not address the nature of this effect, but it may be a result of the rate determining step not being formation of the π-complex, but rearrangement to the σ-complex and its subsequent deprotonation. $Cp^*_2ScCH_3$ has a k_H/k_D for the reaction with benzene of 2.9 (vide supra).

From the reactions of Cp^*_2ScR (R = hydride, alkyl, aryl) complexes with hydrocarbons a reasonable picture can be drawn of the transition state for this metathesis reaction. A k_H/k_D of 2.9 for the reaction of $Cp^*_2ScCH_3$ with benzene indicates that there must be some C-H bond weakening in the transition state. The lack of a significant substituent effect in the reactions of $Cp^*_2ScCH_3$ with either arenes or styrenes suggests that the transition state for this reaction is no more polar than the ground state. Homolytic bond cleavage, as in radical chain type processes, is also excluded, since ring opening of cyclopropane is not observed after long reaction times, and because activation of solvent is never observed. When $Cp^*_2ScCH_3$ is pyrolyzed in C_6D_{12}, only CH_4 is observed (no CH_3D). If Sc-CH_3 bonds were being homolytically cleaved under the reaction conditions, some activation of solvent, giving CH_3D, would be expected. The large negative entropy of activation for the reactions of $Cp^*_2ScCH_3$ with styrenes suggests that the transition state is highly ordered, and that the rate

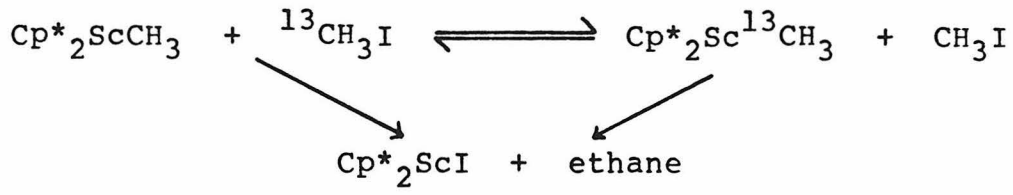
determining step is an associative one. The transition state that best fits our observations is a nonpolar 4-centered one, shown below.



R = hydride, alkyl, aryl; A-B = H-H, C-H

The formation of significant amounts of $Cp^*_2ScCH_2C_6H_5$ in the reaction of $Cp^*_2ScCH_3$ with toluene suggests that coordination of the π cloud of the arene is not along the reaction coordinate for these reactions. The lack of substituent effects in the reactions of styrenes and arenes with $Cp^*_2ScCH_3$ are also strong evidence that initial attack of Sc on the π systems of these substrates is not important in C-H activation. This result is particularly significant, since coordination of the π system prior to C-H activation is thought to occur in virtually every reaction of organometallic complexes with sp^2 C-H bonds.[44]

Reactions of Permethylscandocene Alkyl Complexes with Alkylhalides. In a reaction reminiscent of the reaction of $Cp^*_2ScCH_3$ with $^{13}CH_4$ (eq 14), $Cp^*_2ScCH_3$ reacts with $^{13}CH_3I$ to give a labeled scandium-methyl complex (Scheme 5).



Scheme 5

An additional reaction is observed that leads to coupling of two methyl groups, forming Cp^*_2ScI and ethane, which is irreversible. These two reactions proceed at comparable rates, both having half-lives of ca. 30 hours at room temperature, when 7 equivalents of methyl iodide are used. The reaction leading to Cp^*_2ScI and ethane is definitely the thermodynamically preferred one. The methyl exchange reaction is thermoneutral, since the only differences between the reactants and the products are isotopic changes. The methyl coupling reaction, however, involves cleavage of $Cp^*_2Sc-CH_3$ and $I-{}^{13}CH_3$ bonds, and formation of Cp^*_2Sc-I and $CH_3-{}^{13}CH_3$ bonds. In general, early transition metal-halide bonds are 20-40 kcal/mole stronger than metal-methyl bonds,[45] and the carbon-carbon bond of ethane is 33 kcal/mole stronger than the carbon-iodine bond of methyl iodide.[16] From these bond strengths an enthalpy of 50-70 kcal/mole is expected for this reaction; with an enthalpy this large it is not surprising that the methyl coupling reaction is irreversible.

An alkyl exchange reaction is also observed in the reaction of $Cp^*_2ScCH_2CH_3$ with CH_3I (eq 22)

$$Cp^*_2ScCH_2CH_3 + CH_3I \xrightarrow[25^oC]{} Cp^*_2ScCH_3 + ICH_2CH_3 \quad (22)$$

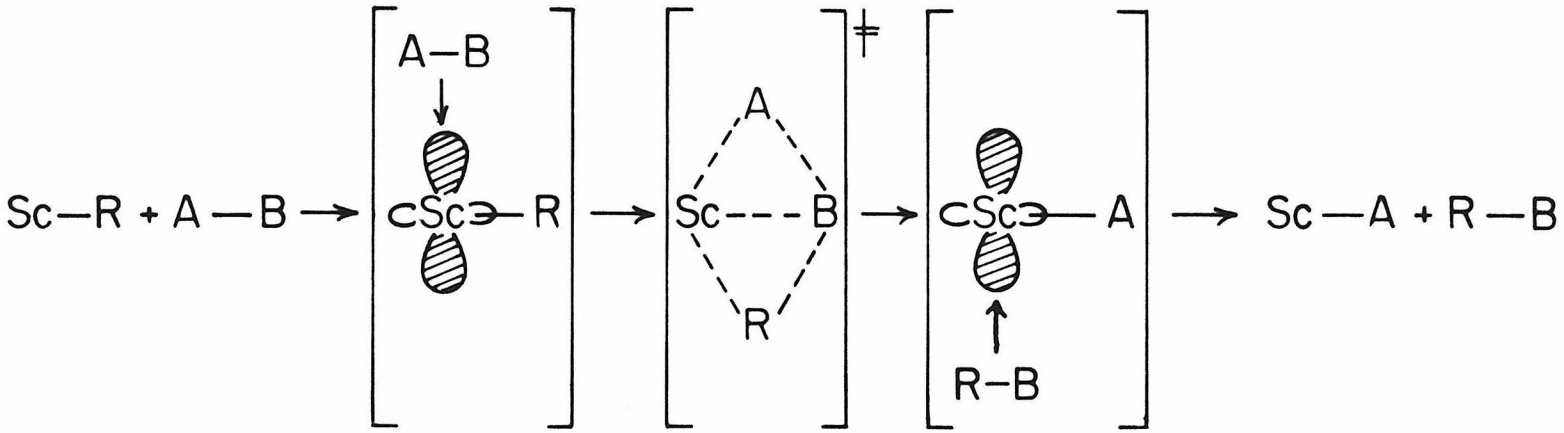
An alkyl coupling reaction between $Cp^*_2ScCH_2CH_3$ and CH_3I, to generate propane, is not observed. Rather, the $Cp^*_2ScCH_3$ produced reacts with CH_3I to give Cp^*_2ScI and ethane. For $Cp^*_2ScCH_2CH_3$, alkyl exchange with CH_3I is more facile than alkyl coupling.

$Cp^*_2ScCH_3$ reacts with benzylchloride and benzylbromide to give only the corresponding Cp^*_2ScX complex (X = Cl, Br) and ethylbenzene (eq 23). Benzylbromide reacts faster than benzylchloride.

$$Cp^*_2ScCH_3 + XCH_2C_6H_5 \xrightarrow[25^oC]{X = Cl, Br} Cp^*_2ScX + CH_3CH_2C_6H_5 \quad (23)$$

<u>σ-bond Metathesis.</u> In the preceding sections we have shown that σ-bond metathesis reactions are common in the chemistry of Cp^*_2ScR complexes (R = hydride, alkyl, aryl). The mechanisms of these reactions are important in understanding the reaction chemistry of scandium complexes. And in a broad sense, these mechanisms will help in understanding the reaction chemistry of all oxidatively inert, highly electrophilic, early transition metal, lanthanide and actinide complexes. From our studies we can draw a fairly detailed picture of the reaction paths for σ-bond metathesis, and discuss factors effecting the rates and product distributions of these reactions.

In several cases σ-bond metathesis reactions are readily reversible, such as the reaction of Cp^*_2ScH with benzene (eq 7) and H/D exchange catalyzed by Cp^*_2ScH. From the studies of C-H bond activation by $Cp^*_2ScCH_3$, a great deal has been learned about the mechanism of σ-bond metathesis. Kinetic measurements suggest that σ-bond metathesis reactions of C-H bonds are associative with highly ordered transition states. Moreover, the observation of a deuterium isotope effect on the rate of the reaction between $Cp^*_2ScCH_3$ and benzene implies that C-H bond weakening is involved in the rate determining step. Any mechanisms for this reaction that include oxidative addition or reductive elimination steps can be excluded, because scandium has no readily available oxidation states other than III. The proposed mechanism, consistent with all the data observations, is shown in Figure 10. The initial interaction is between the bond being activated (A-B) and the LUMO of the electrophilic scandium complex, as in C. This donation from the A-B bond to the empty metal orbital is similar to an agostic interaction (A-B = C-H). This intermediate does not lie in a well on the potential surface, since it does not build up. We have been unable to observe an agostic ground state for any permethylscandocene-based complexes (vide supra), indicating that this interaction should be weak. C leads to the 4-centered transition state D, which cleaves to give products (through C').



C D C′

Figure 10. Proposed mechanism for σ-bond metathesis. R = H, alkyl, aryl; A-B = H-H, C-H, C-X, X-C; X = halide. The orbital pictured in C and C' is the $1a_1$ orbital.[47]

The high electrophilicity of the metal center is very important in these σ-bond metathesis reactions. The reactant A-B bond is activated by interaction with a vacant metal orbital (as in C), and it is the high electrophilicity of the early transition metal that brings about interactions with such weak donor bonds as H-H and C-H. σ-bond metathesis is formally a $[2_s + 2_s]$ reaction which is symmetry disallowed.[46] By inclusion of the vacant metal orbital, the transition state becomes that of a $[2_s + 2_s + d]$ reaction, which is allowed. The d orbital may be either the $1a_1$ or the b_2 orbital.[47] The mechanism of Figure 1 is drawn with the $1a_1$ orbital as the interacting vacant metal orbital, because the $1a_1$ is the LUMO of Cp^*_2ScR. It should be stressed that although high electrophilicity of the metal center drives the reaction, it does not greatly polarize or heterolytically cleave the bond being activated. Rather, activation of the A-B bond leads to a 4-centered rather nonpolar transition state.

Both thermodynamic and kinetic effects govern the outcome of the σ-bond metathesis reaction. The energy of the transition state is strongly dependent on the the ability of the members of this 4-centered interaction to participate in multicenter bridging interactions. Scandium's d orbitals are suitably disposed to allow good overlap with the other groups in B, but the non-metal atoms (R, A and B) must use s and p orbitals for these bridging interactions. The s or-

bital, being spherically symmetric, is the best suited for this type of interaction, since its nondirectional nature allows significant overlap with two orbital in very different directions (e.g. the bridging hydrides of B_2H_6). It is, therefore, not surprising that one of the fastest σ-bond metathesis reactions is between Cp^*_2ScH and H_2 ($k_{obs} > 10^3$ $M^{-1}sec^{-1}$ at -95^oC). The transition state for this reaction should have the best orbital overlap (hence most bonding and lowest energy) possible for this type of metathesis reaction, since all three of the non-metal atoms utilize spherically symmetric (1s) orbitals in bonding. The reactions of Cp^*_2ScR complexes (R = alkyl, aryl) with H_2 are also very facile (R = CH_3, half-life < 5 min. at -78^oC), which may be a result of the high degree of orbital overlap of the two H atom 1s orbitals in the transition state. In cases where s and p character are mixed (e.g. C-H), the degree of s character is important. In the same way that s orbitals bridge better than p orbitals, so a carbon orbital with high s character have better overlap in the bridging position than one with low s character, because the carbon orbital with more s character will be less directional in nature. The result of this is that σ-bond metathesis reactions between Cp^*_2Sc-R and C-H bonds will be the fastest for C-H with the highest s character ($sp > sp^2 > sp^3$). This trend can be seen in the rates of C-H activation by $Cp^*_2ScCH_3$ (H-C CCH_3 (sp) > H-CH=CHC_6H_4X and arene (sp^2) >

$H\text{-}CH_2C_5(CH_3)_4$ (sp^3)) and in the rates of H/D exchange catalyzed by Cp^*_2ScH (C-H (sp^2) > C-H (sp^3)). This preference for C-H bonds with higher degrees of s character is also seen in the reaction of $Cp^*_2ScCH_2CH(CH_3)_2$ with propene (eq 17). The sp^2 vinylic C-H is chosen exclusively over the sp^3 allylic one, even though the allylic C-H is weaker and activation of it would lead to the stable η^3-allylic complex, $Cp^*_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$.

It is interesting to note that when Cp^*_2ScR (R = hydride, methyl) can react with with orbitals of all p character (π bonds of $HC{\equiv}CCH_3$) or an sp C-H bond ($H\text{-}C{\equiv}CCH_3$), only the σ-bond metathesis reaction is observed, even though alkyne insertion reactions are facile in this system (vide infra).

In the reactions of Cp^*_2ScR complexes (R = alkyl, aryl) with C-H bonds, products resulting from C-C bond coupling are never observed. The reason may be kinetic or thermodynamic or both. For the reactions of Cp^*_2ScR (R = alkyl) with benzene the thermodynamics can be calculated. Since the relative bond strengths of scandium-hydride versus scandium-phenyl bonds are known, a direct comparison of the enthalpies of alkyl-aryl exchange reactions (Scheme 6(a)) and alkyl-aryl coupling reactions (Scheme 6(b)) to be made.

$$Cp^*_2ScCH_3 + H\text{-}C_6H_5 \longrightarrow \underset{(x)}{Cp^*_2Sc\text{-}C_6H_5} + \underset{(105)}{H\text{-}CH_3} \qquad (a)$$

$$Cp^*_2ScCH_3 + H\text{-}C_6H_5 \longrightarrow \underset{(x+1.5)}{Cp^*_2Sc\text{-}H} + \underset{(101)}{CH_3\text{-}C_6H_5} \qquad (b)$$

Scheme 6: alkyl-aryl exchange (a) and alkyl-aryl coupling (b) reactions. The numbers in parentheses represent the bond strength (kcal/mole) of the bond above them.

Since both reactions cleave the same bonds in the reactants, the difference in enthalpies of the two reactions is a result of the different energies of the products. From the bond strengths given in Scheme 6, the alkyl-aryl exchange reaction is 2.5 kcal/mole more exothermic than the alkyl-aryl coupling reaction, i.e. the thermodynamically preferred reaction is alkyl-aryl exchange (assuming that the two reactions have comparable entropies). If the methyl ligand of $Cp^*_2ScCH_3$ is replaced with an n-butyl one, the relative enthalpies of alkyl-aryl exchange (Scheme 7(a)) and alkyl-aryl coupling (Scheme 7(b)) can be calculated for the reaction with benzene.

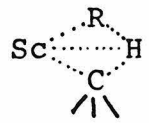
$$Cp^*_2Sc\text{-}C_4H_9 + H\text{-}C_6H_5 \longrightarrow \underset{(x)}{Cp^*_2Sc\text{-}C_6H_5} + \underset{(98)}{H\text{-}C_4H_9} \qquad (a)$$

$$Cp^*_2Sc\text{-}C_4H_9 + H\text{-}C_6H_5 \longrightarrow \underset{(x+1.5)}{Cp^*_2Sc\text{-}H} + \underset{(98)}{C_4H_9\text{-}C_6H_5} \qquad (b)$$

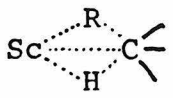
Scheme 7: alkyl-aryl exchange (a) and alkyl-aryl coupling (b) reactions. The numbers in parenthesis represent the bond strength (kcal/mole) of the bond above them.

The bonds formed in the two different organic products (butane and butylbenzene) have equal energies,[17] thus the enthalpies of these two reactions differ by 1.5 kcal/mole, with the alkyl-aryl coupling reaction (Scheme 7(b)) being thermodynamically preferred over alkyl-aryl exchange (again, assuming comparable entropies for the two reactions). In the reaction of $Cp^*_2ScC_4H_9$ with benzene, however, the only products formed are $Cp^*_2ScC_6H_5$ and butane; no butylbenzene is observed. The fact that only a single reaction path (Scheme 7(a)) is operative indicates that there must be a kinetic preference for alkyl-aryl exchange. We do not have reliable bond strength data to calculate the enthalpies of activation of non-arene C-H bonds, so we can not determine what type of reaction (alkyl exchange or alkyl coupling) is thermodynamically preferred. It is important to note however, that C-C bond formation is never observed in any C-H bond activation reactions by Cp^*_2ScR complexes (R = alkyl, aryl); for example, when $Cp^*_2ScCH_3$ is treated with $^{13}CH_4$, only methyl exchange is observed, ethane is not formed.

The nature of this kinetic preference for exchange over coupling in the reactions of Cp^*_2ScR complexes with C-H bonds may be found in the structure of the transition state. The exchange (D1) and coupling (D2) transition states differ only in the orientation of the incoming C-H group.



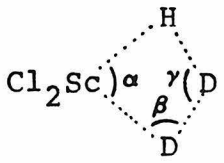
D1



D2

The fact that exchange is the kinetically preferred pathway, indicates that D1 must be lower in energy than D2, which is probably a result of the overlap for the atom in the central bridging position being the most sensitive to s character. In D1 the hydrogen occupies this central position and can bridge the three atoms very aptly with its nondirectional 1s orbital. In D2, however, this central bridging position is occupied by a far more directional carbon orbital (sp, sp^2 or sp^3) which can not bridge as well as the hydrogen.

A preference for the better bridging ligand in the central position is consistent with calculations done by Steigerwald and Goddard on a related system.[48] They predicted the structure of the transition state (Figure 11) for the H/D exchange reaction between Cl_2ScH and D_2.



$\alpha = 62^{\circ}$

$\beta = 75^{\circ}$

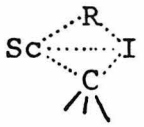
$\gamma = 149^{\circ}$

Figure 11: the predicted transition state for the H/D exchange reaction between Cl_2ScH and D_2.

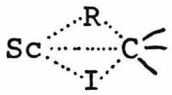
The angle that the central D must bridge (142°) is far greater than that of the lateral D (75°). It is expected for the better bridging ligand to occupy the site with the most obtuse bridging angle.

This kinetic preference for D1 must be large, because D1 has far more severe steric interactions. In D1 both of the organic groups are forced into the edges of the wedge of the Cp* ligands, where they are be involved in unfavorable steric interactions. In D2 one of the organic groups is forced into the wedge, but the other sits is the center, which is the least sterically crowded position in the molecule. These steric effects are most likely responsible for the kinetic selectivity for 1° over 2° C-H bonds. For example, at 80°C $Cp^*_2ScCH_3$ reacts with styrenyl C-H bonds roughly two orders of magnitude faster than with arene C-H bonds.

In the reaction of $Cp^*_2ScCH_3$ with $^{13}CH_3I$ both alkyl exchange and alkyl coupling reactions were observed (Scheme 8) at comparable rates, with the latter being the thermodynamically favored by roughly 60 kcal/mole. The proposed transition states for these two processes are D3 and D4, respectively.



D3



D4

By the previous logic, D3 should be preferred over D4, because the lower energy transition state has the best bridging ligand in the central position. The reason that the D3 and D4 are so close in energy may be due to a strong scandium iodine interaction in D4. Donation of electron density from one of the iodine lone pairs into the remaining empty orbital on scandium would strengthen the scandium iodine interaction in D4. If the la_1 were the vacant orbital in the transition state,[49] the iodine lone pairs would have poorer overlap with it in D3 than in D4, thus D4 would be lowered in energy relative to D3. This type of donation would be impossible for hydrogen, so no such stabilization would be expected for C-H bonds. This hypothesis explains the faster rate for benzylbromide over benzylchloride in their reaction with $Cp^*_2ScCH_3$ (eq 23). The bromine should have more diffuse lone pairs, allowing for greater donation and lowering of the energy of the transition state. The fact that carbon-bromine bonds are weaker than carbon-chlorine bonds may also explain the rate difference.

EXPERIMENTAL

General Considerations. All manipulations were carried out using either high vacuum line or glove box techniques. All solvents were purified by distillation from Na or CaH_2 followed by vacuum transfer from titanocene. $^{13}CH_4$ (Merck or Stohler, ca. 10% $^{12}CH_4$ and 90% $^{13}CH_4$) was dried over potassium and treated with a heterogeneous nickel phoshine complex to remove H_2 and O_2. All other gaseous reagents were freeze-pump-thawed twice before use. All liquid reagents were dried over 4A molecular sieves, and freeze-pump-thawed twice before use. NMR solvents, d_6-benzene and d_{12}-cyclohexane, were vacuum transferred from activated 4Å molecular sieves, then from titanocene.

^1H NMR spectra were run on Varian EM-390 (continuous wave, 90 MHz), JOEL FX-90Q (fourier transform, 90 MHz) and Brucker WM500 (fourier transform, 500 MHz) spectrometers. All spectra of new compounds are listed in Table 7. Infrared spectra were run as nujul mulls on KBr plates and recorded on a Beckman IR-2420 spectrometer. Mass spectra were recorded using a Kratos MS25 spectrometer. Analyses were performed by the Caltech Analytical Laboratory.

Many of the reactions in this chapter were carried out in NMR tubes. Any experiment discussed in this chapter and not listed below was carried out in a sealed NMR tube with ca. 20 mg of the scandium complex in ca.

Table 7. ^{1}H and ^{13}C NMR spectroscopic data.*

Compound	Assignment	δ (ppm)	Coupling
$[Cp^*Sc(\eta^5\text{-}C_5(CH_3)_4CH_2]_x$	a	1.97 s	
	b	2.07 s	
a b c	b	1.53 s	
	c	1.50 s	
$Cp^*_2Sc\text{-}CH{=}CH\text{-}C_6H_4\text{-}CH_3$	a	1.88 s	
	b	8.07 d	20
a b c d	b	6.43 d	20
	c	7.58 d	8
	c	7.20 d	8
	d	2.27 d	
$Cp^*_2Sc\text{-}CH{=}CH\text{-}C_6H_4\text{-}OCH_3$	a	1.88 s	
	b	7.90 d	20
a b c d	b	6.35 d	20
	c	7.51 d	8
	c	6.92 d	8
	d	3.45 d	

Compound	Assignment	δ (ppm)	Coupling
$Cp^*_2Sc-\underbrace{CH=CH}-C_6H_4-CF_3$ (a, b, c)	a	1.88 s	
	b	8.19 d	21
	b	6.37 d	21
	c	7.51 m	
$Cp^*_2ScC\equiv CCH_3$ (a, b)	a	2.00 s	
	b	2.07 s	

* Unless otherwise specified, spectra were taken in C_6D_6 at ambient temperature at 90 Mhz. The chemical shifts are reported in relative to TMS or residual protons of the solvent. Coupling constants are reported in Hz.

0.35 mL of d_6-benzene. The spectra were referenced to internal TMS or the protio impurity of the solvent (C_6D_5H). A measured amount of the appropriate reagent was added to the tube before it was cooled to 196°C and sealed with a torch. Cyclooctane was used as an integration reference (when needed) because of its low volatility and inertness toward reactions with scandium.

Data analysis and plotting were carried out with a Compaq Deskpro minicomputer. Weighted least squares fitting techniques were used to calculate slopes and errors [50] of the van't Hoff, kinetic and Arrhenius plots. The error in a given data point was estimated by repeated measurement of that data point.

Preparation of X. $Cp^*_2ScCH_3$ (0.50 g, 1.5 mmol) was dissolved in 5 mL of cyclohexane and the resulting solution heated to 80°C for 4 days. Large yellow crystals of X were isolated from the mother liquor by filtration, and washed several times with petroleum ether. The crystals were dried in vacuo (0.40 g, 85%). Anal. calc. for $C_{20}H_{29}Sc$: C, 76.40; H, 9.30. Found: C, 75.42; H, 9.04.

Preparation of $Cp^*_2ScCH{=}CHC_6H_4CH_3$-p. We were unable to isolate the scandium styrenyl complexes made with para-methoxy- or para-CF_3-styrene as solids. We were able to isolate $Cp^*_2ScCH{=}CHC_6H_4CH_3$-p and its synthesis is described here. $Cp^*_2ScCH_3$ (256 mg, 0.77 mmol) and para-

methyl-styrene (91 L, 1.01 equivalents) were dissolved in 4 mL of petroleum ether. This solution was heated to 63°C for 12 hours and concentrated to 2 mL. Cooling the solution to -78°C precipitated 99 mg (30% yield) of the pale yellow product. IR data (cm^{-1}): 2710(w), 1503(s), 1193(w), 1138(w), 1102(s), 1055(m), 1020(m), 981(m), 835(m), 754(m), 656(s), 608(w), 585(w), 480(s), 365(m). Anal. calc. for $C_{29}H_{39}Sc$: C, 80.52; H, 9.09. Found: C, 80.29; H, 9.20.

Preparation of $Cp^*_2ScC{\equiv}CCH_3$. $Cp^*_2ScCH_3$ (234 mg, 0.71 mmol) was dissolved in 10 mL of petroleum ether and the resulting solution was cooled to -78°C. Propyne (0.78 mmol) was condensed into the solution from a gas bulb, and the reaction vessel was then slowly warmed to room temperature. The reaction mixture was concentrated to 4 mL. Cooling the solution to -78°C precipitated the white solid product (115 mg, 62%), which was isolated by filtration. IR data (cm^{-1}): 2720(w), 2090(s), 1165(w), 1060(w), 1022(m), 965(s), 800(w), 700(w), 655(w), 440(s), 370(m). Anal. calc. for $C_{23}H_{33}Sc$: C, 77.93; H, 9.38. Found: C, 77.83; H, 9.42.

Preparation of d_{30}-$Cp^*_2ScCH_3$. A 50-mL thick walled glasss bomb was charged with 4 g of $Cp^*_2ScCH_3$ (12 mmol), 10 mL of C_6D_6 (99.5% D) and two atmospheres of D_2. The bomb was thermolyzed at 80°C for one day and the gas

(hydrogen/methane) removed *in vacuo*. Approximately one atmosphere of D_2 was then added to 115°C for 24 hours. The $H_2/HD/D_2$ and benzene were removed *in vacuo* and replaced with fresh C_6D_6 (20 mL) and D_2 (1 atm). The bomb was then thermolyzed at 115°C for 24 hours. This cycle was repeated with 35 mL of C_6D_6 and D_2 (1 atm). The bomb was cooled to -78°C and 12 mmol of CH_2Cl_2 and one atmosphere of H_2 added. After warming to room temperature the benzene solution was stirred for 5 minutes and volatiles removed *in vacuo*. Petroleum ether (10 mL) was added to the resulting solid and the slurry filtered. The remaining solid was washed twice with petroleum ether, and all of the petroleum ether solutions combined. The petroleum ether was removed *in vacuo* and replaced with 5 mL of diethylether. Cooling the diethylether solution to -78°C precipitated 2.73 g (62%) of the yellow product, d_{30}-Cp^*_2ScCl. The proton impurity of d_{30}-Cp^*_2ScCl was measured by ^1H NMR integration of its Cp* resonance relative to ferrocene, and found to be <0.2%. d_{30}-$Cp^*_2ScCH_3$ ws prepared from d_{30}-Cp^*_2ScCl by a method previously discussed (Chapter 1).

$Cp^*_2ScD + CH_3I$ in C_6H_6 (Eq. 4). Cp^*_2ScD is not stable for long periods as a solid, but can be isolated. $Cp^*_2ScCH_2C_6H_5$ (33 mg, 0.081 mmol) was dissolved in 0.3 mL of C_6D_6 and two atmospheres of D_2 put over the solution. After being stirred for ten minutes the benzene solution

was cooled to -78°C and the benzene sublimed out of the reaction vessel in vacuo. C_6H_6 (Ø.4 mL) was added to the resulting solid and the cloudy solution transferred to an NMR tube. After 5 minutes at room temperature, the tube was cooled to -78°C and Ø.Ø98 mmol of CH_3I was transferred into the tube. The tube was sealed with a torch and warmed to room temperature. As the benzene melted, gas bubbled out of solution. The ^1H NMR showed resonances assignable to Cp^*_2ScI and CH_4; CH_3D was not observed in this spectrum. A small amount of $Cp^*_2ScC_6H_5$ (5% relative to Cp^*_2ScI) was also observed.

Cyclopentane H/D Exchange. We could not find an integration reference that did not undergo H/D exchange under the conditions required to promote H/D exchange into cyclopentane, so the extent of deuterium incorporation was measured by mass spectroscopy. A 2 mL sealable tube was charged with 8 mg of $Cp^*_2ScCH_3$ (Ø.Ø24 mmol), 5Ø L of cyclopentane (Ø.53 mmol), Ø.35 mL of C_6D_6 and 7ØØ torr of H_2. The entire tube was cooled to -196°C and sealed with a torch, giving the sample 3.6 atmospheres of H_2 at 25°C. The entire tube was thermolyzed at 12Ø°C for 26 days, and the reaction solution examined by G. C. mass spectroscopy. By comparison of the mass spectrum of cyclopentane from this reaction to that of normal cyclopentane, it was determined that the cyclopentane from this reaction was 17% enriched in deuterium, giving a turnover rate of Ø.Ø6

turnovers/day.

Measurement of Equilibrium Constants for Eqs. (7) and (8). The sample used to study the equilibrium between Cp^*_2ScH and $Cp^*_2ScC_6H_5$ (Eq. (7)) was prepared in an NMR tube mounted directly on a Kontes teflon stoppered valve. This tube was charged with 18 mg of $Cp^*_2ScCH_3$ (0.054 mmol) and 0.5 mL of C_6H_6. The entire tube (up to the Kontes valve) was cooled to -196°C, and evacuated. H_2 (700 torr) was admitted into the tube and ten minutes allowed for the gas to come to thermal equilibrium. The Kontes valve was closed and the tube warmed to room temperature. The apparatus was removed from the vacuum line and shaken for five minutes to ensure formation of Cp^*_2ScH. The tube was then cooled to -196°C, the hydrogen removed in vacuo, and the tube sealed with a torch.

The sample used to study the equilibration between $Cp^*_2Sc(THF)H$ and C_6H_6 (Eq. (8)) was prepared by dissolving an isolated sample of $Cp^*_2Sc(THF)H$ in C_6H_6 solvent in an NMR tube and sealing it with a torch.

The 25°C and higher temperature experiments were carried out in a constant temperature oil bath, which was heated with a Precision Scientific Co. thermostated water circulator. In this way the temperature of the oil bath was kept constant to ± 0.1°C. The samples were fully submerged in the bath and agitated to facilitate the

equilibration of H_2 between the solution and gas phases. The experiments carried out at 6°C were performed in a room cooled to this temperature. At a given temperature, the volume at the solution and the ratio of the two equilibrating scandium species (^{1}H NMR) were measured.

The equation describing the equilibrium constant for Eq. (7) is shown below.

$$K_{eq} = \frac{[Cp^*_2ScC_6H_5][H_2]}{[Cp^*_2ScH][C_6H_6]}$$

The relative concentrations of the two scandium complexes were calculated from the ratio of their Cp* peak heights. The concentration of benzene was calculated from its density at the temperature of the experiment. The concentration of hydrogen was calculated using Henry's law and the standard concentration of H_2 at the temperature of the experiment.[ ] To derive the expression for $[H_2]_{equil}$, two simultaneous equations were solved (Eqs. (28) and (29)).

$$(\text{mmol } H_2)_{tot} = A\left(\frac{V_1}{RT}\right) + B\,(V_2) \tag{28}$$

$$B = A\left(\frac{[H_2]_{std}}{1 \text{ atm}}\right) \tag{29}$$

Where A is the pressure of H_2 above the solution, V_1 is the volume of gas space above the solution, R is the gas constant, T is the temperature, B is the concentration of H_2 in solution, V_2 is the volume of the solution and $[H_2]_{std}$ is the concentration of H_2 in C_6H_6 at a temperature T when the pressure of H_2 is one atmosphere. [51] The expression for $[H_2]_{equil}$ (B) is given in Eq. (30).

$$[H_2]_{equil} = \frac{(\text{total mmol } H_2)}{\frac{V_1}{[H_2]_{std} RT} + V_2} \qquad (30)$$

The total mmol of H_2 is given by Eq. (31).

$$\text{total mmol } H_2 = (\text{mmol } H_2)_{initial} + \text{mmol } Cp^*_2ScC_6H_5 \qquad (31)$$

The $(\text{mmol of } H_2)_{initial}$ was calculated using Eq. (30), assuming that only that amount of H_2 in the known volume of benzene would remain after evacuation of the sample tube (just prior to sealing). The equilibrium constants for Eq. (8) were determined using analogous calculations.

Kinetic Measurements of the Reaction of $CP^*_2ScCH_3$ with C_6H_6 and C_6D_6. These reactions were carried out in neat benzene solutions. Sealed NMR tubes were prepared with 25 mg $Cp^*_2ScCH_3$ 0.4 mL of benzene and 3 μL of cyclooctane, and thermolyzed at 80°C. The progress of the reaction was followed by ^1H NMR (continuous wave, Varian EM-390), monitoring the integrated intensity of Sc-CH_3 versus internal cyclooctane. The reaction of $Cp^*_2ScCH_3$ with C_6H_6 gave linear first order kinetic plots while the reaction with C_6D_6 gave nonlinear first order plots. The interpretation of these kinetics is discussed in the text. The ratio of CH_3D to CH_4 was measured by cutting and weighing the peaks of the 500 MHz NMR spectrum.

Reaction of X with CD_4. A sealable NMR tube was charged with 16 mg of X and 0.40 mL of C_6D_{12}. The entire tube was cooled to -78°C and evacuated. CD_4 (400 torr, ca. 1.5 equivalents) was admitted to the tube and the tube sealed. In the initial NMR spectrum, no signal was observed between 0 and 0.5 ppm. After thermolysis at 80°C for eight days, a resonance at ca. 0.15 ppm was observed (CH_4 appears at 0.15 ppm in C_6D_{12}). This resonance grew on further heating, until after 35 days it was >50% CH_4.

Kinetic Measurements of Intramolecular C-H and C-D Activation. $Cp^*_2ScCH_3$ (25 mg, 0.076 mmol), 3 μL cyclooctane and 0.40 mL of C_6D_{12} were loaded into a sealable NMR tube, and the tube sealed under 1 atm of N_2.

The sample was thermolyzed at 80°C. The kinetics of intramolecular C-H activation (Eq. (11)) were followed by ^1H NMR monitoring the decrease in integrated intensity of the Sc-CH_3 resonance relative to internal cyclooctane. The kinetics of intramolecular C-D activation were examined using a directly analogous experiment, except d_{30}-$Cp^*_2ScCH_3$ was substituted for $Cp^*_2ScCH_3$. Both of these reactions gave non-first order kinetics. The interpretation of their kinetic behavior is discussed in the text.

Kinetic Measurements of the Reaction of d_{30}-$Cp^*_2ScCH_3$ with C_6H_6 and C_6D_6. These measurements were made in a manner directly analogous to those described for the reactions of $Cp^*_2ScCH_3$ with benzene, except d_{30}-Cp_2ScCH_3 was substituted for $Cp^*_2ScCH_3$. The reactions of d_{30}-$Cp^*_2ScCH_3$ with C_6H_6 and C_6D_6 both obey first order kinetics, giving pseudo first order rate constants of $(1.41 \pm 0.05) \times 10^{-4}$ sec^{-1} and $(5.1 \pm 0.1) \times 10^{-5}$ sec^{-1}, respectively. The true value of k_H/k_D is discussed in the text.

Kinetic Measurements of the Reaction of $Cp^*_2ScCH_3$ with $^{13}CH_4$. Kinetic samples were prepared in 5-mm medium walled NMR tubes (Wilmad Inc., 524-p), which contained 10 mg of $Cp^*_2ScCH_3$ (0.03 mmol), C_6D_{12} (0.5 mL) and 0.6-5.0 mmol of $^{13}CH_4$. At 70°C, approximately 20% of the CH_4

was in solution; accurate (±5%) concentrations were obtained with cyclooctane as an internal integration standard. Plots of $-\ln[Sc-CH_3]$ versus time should be linear over 2-4 half-lives (depending on the ratio of ^{12}C to ^{13}C in the system) in these experiments with excess $^{13}CH_4$. Typically only data from the first 20-30% of the reaction was used. A value of 1×10^{-5} $M^{-1}sec^{-1}$ was obtained for the second order rate constant. In roughly 20% of these experiments k_{obs} was 3-4 times larger than expected. Repeating the experiment generally gave a value of k_{obs} consistent with those observed at other concentrations of methane. We attribute this rate increase to a small amount of some catalyst promoting the reaction. The identity of this catalyst is unknown, but the reaction chemistry exhibited by the tuck-in complex (X) (*vide supra*) suggests that it may be a likely candidate. This apparent catalysis was most common in aged sample of $Cp^*_2ScCH_3$, in which some thermal decomposition could have given rise to a small amount of **X**.

Kinetic Measurements of the Reactions of $Cp^*_2ScCH_3$ with $H_2C=CHC_6H_4X$-p (X=CF_3, OCH_3). Kinetic samples in septum capped NMR tubes contained 25 mg of $Cp^*_2ScCH_3$ (0.076 mmol), 0.4 mL of C_6D_6 and 0.16-0.30 mmol of the appropriate styrene compound. The kinetics of the reaction of $Cp^*_2ScCH_3$ with $H_2C=CHC_6H_4OCH_3$-p were followed

by ^{1}H NMR (FT NMR, JOEL FX-90Q), monitoring the disappearance of the Sc-CH_3 signal and the appearance of the methoxy resonance of $Cp^*_2ScCH=CHC_6H_4OCH_3$ relative to internal $FeCp_2$ (sublimed twice). The kinetics of the reaction of $Cp^*_2ScCH_3$ with $H_2C=CHC_6H_4CF_3$-p were followed by F^{19} NMR (FT NMR, JEOL FX-90Q), monitoring the disappearance of the CF_3 resonance of $H_2C=CHC_6H_4CF_3$-p and the appearance of the CF_3 signal of $Cp^*_2ScCH=CHC_6H_4CF_3$-p relative to internal $C_6H_5CF_3$. This reaction was followed by ^{1}H NMR as well, to verify that only $Cp^*_2ScCH=CHC_6H_4$-CF_3 was produced. The reactions of $Cp^*_2ScCH_3$ with both of these styrenes obey second order kinetics, [31] giving linear second order plots (Fig. 7) for over three half-lives. The Arrhenius and activation parameters were calculated using standard equations and are given in Table 6. The Arrhenius plots are shown in Fig. 8. Both reactions exhibit small enthalpies of activation and large negative entropies of activation, indicative of an associative reaction, going through a highly ordered transition state. The similarity of the activation parameters for these reactions suggest that substituent effects are unimportant in these reactions.

Kinetics of the Reactions of d_{30}-$Cp^*_2ScCH_3$ with C_6H_5R (R=$N(CH_3)_2$, CH_3, H, CF_3). Sealed NMR tubes containing 15 mg d_{30}-$Cp^*_2ScCH_3$ (0.041 mmol), 0.35 mL of C_6D_{12}, 0.52 mmol of the appropriate substituted benzene

and 2.5 μL of cyclooctane were thermolyzed at 80 0.5°C. The reaction was followed by ^{1}H NMR, monitoring the decrease in integrated intensity of the Sc-CH_3 resonance relative to cyclooctane. In all cases, only phenyl complexes were observed, and the kinetics were pseudo first order (Fig. 9) for over three half-lives. CH_3D accounts for 5% or less of the total methanes produced. The rate constants for these reactions are given in Table 5.

Reaction of Cp^*_2ScR(R=CH_3, $CH_2C_6H_5$, $C_6H_4CH_3$-o,-p) with Toluene. A glass reaction vessel with a Kontes teflon valve was charged with 20 mg of Cp^*_2ScR (eq. 0.05 mmol) and 5 mL of toluene. The entire vessel was then immersed in an oil bath at the prescribed temperature for the prescribed time period. The toluene solvent was removed *in vacuo* and the resulting solid dissolved in C_6D_6. The products of the reaction were identified by 500 MHz ^{1}H NMR. The product ratios are given in Table 8.

The Reaction of $Cp^*_2ScCH_3$ with Methyliodide. A sealable NMR tube was charged with 15 mg $Cp^*_2ScCH_3$ (0.045 mmol), 0.4 mL of C_6D_6 and 0.27 mmol of $^{13}CH_3I$. The tube was sealed with a torch and the reaction followed by ^{1}H NMR. Initially only $Cp^*_2Sc^{12}CH_3$ was observed. As the intensity of the Sc-$^{12}CH_3$ signal decreased, resonances for both Sc-$^{13}CH_3$ and ^{13}C labeled ethane were observed. The

approximate half-life for the disappearance of Sc-$^{12}CH_3$ was 5 hours at 25°C. In a second experiment, 15 mg of $Cp^*_2ScCH_3$ was reacted with 0.30 mmol of $^{12}CH_3I$. The resonance of Sc-CH_3 slowly decreased as ethane was being formed. The half-life of this reaction was approximately 30 hours at 25°C, and represents the half-life of only the alkyl coupling reaction, since the alkyl exchange reaction is degenerate in this experiment. Thus, the half-life of alkyl exchange is also roughly 30 hours, because the half-life of the reaction of $Cp^*_2ScCH_3$ with $^{13}CH_3I$ is the sum of the half-lives of the alkyl coupling and alkyl exchange reactions (Scheme 5).

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Insertion and Vinylic C-H Bond Activation Reactions of Unsaturated Hydrocarbons with Permethylscandocene Alkyl and Hydride Complexes.

INTRODUCTION

Early transition metal organometallic complexes are highly reactive toward a wide variety of organic substrates. This high reactivity is thought to be due to the highly electrophilic metal center (usually d^0) and the coordinative unsaturation of these complexes.[1] Some of the most reactive organic substrates are olefins and alkynes, which, being nucleophilic, often react readily with these organometallic electrophiles. Early transition metal complexes catalyze a diverse series of organic reactions for olefins, including isomerization, metathesis, hydrogenation, oligomerization and polymerization.[2]

In the early 1950's Ziegler and his coworkers discovered that $TiCl_4/Al(CH_2CH_3)_3$ is a very efficient ethylene polymerization catalyst.[3] His group and others have found similar catalysts that polymerize several other olefins as well.[4] Understanding the mechanisms of these polymerization reactions is a great challenge. Industrially useful catalysts are generally heterogeneous and polymerize olefins too rapidly to make them convenient for mechanistic study. Several homogeneous titanium catalysts have been developed that polymerize or oligomerize olefins at measurable rates.[5] Extensive mechanistic study of these soluble catalysts indicate that the active polymerization catalysts have a Ti(IV) coordinatively unsaturated metal center.[1(a),

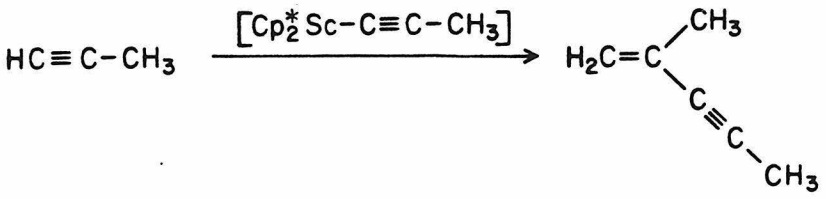
6] Direct observation of individual steps in the polymerization mechanisms of these catalysts is difficult because of competitive reduction of the metal complex and other side reactions leading to deactivation of the catalyst. As a model for this catalyst system, Watson prepared Cp^*_2LuR (R = H, CH_3).[7] Like the proposed active site for Ziegler-Natta catalysis, these complexes are highly electrophilic and coordinatively unsaturated. Both ethylene polymerization and propene oligomerization are catalyzed by Cp^*_2LuR. This lutetium system provides evidence for initiation, propagation and termination steps proposed for Ziegler-Natta catalysis, and is the first system in which the direct product of olefin insertion into a M-C σ-bond has been observed.[8] Several types of termination step are observed in this lutetium system, including β-hydride and β-methyl elimination as well as intramolecular C-H activation of a Cp* ligand.

We have examined the reactions of Cp^*_2ScR (R = H, alkyl) with olefins and alkynes. Previous to our work, the only reported reactions of scandium complexes with olefins were the polymerization of ethylene and oligomerization of propene by $Cp_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$.[9] Although $Cp^*_2ScCH_3$ is isoelectronic with $Cp^*_2LuCH_3$, Sc has a smaller ionic radius than Lu, making steric interactions more severe for Sc. Thus, Cp^*_2ScR complexes polymerize ethylene, but react only stoichiometrically with propene, isobutene and other

olefins. The products of these reactions are vinylic scandium complexes, formed by direct vinylic C-H activation of $H_2C=CHR'$ (R = H, CH_3). Allylic scandium complexes are not observed. Our work suggests in addition to β-hydride elimination and chain transfer, direct vinylic C-H activation may be an active termination step for Ziegler-Natta catalysis.

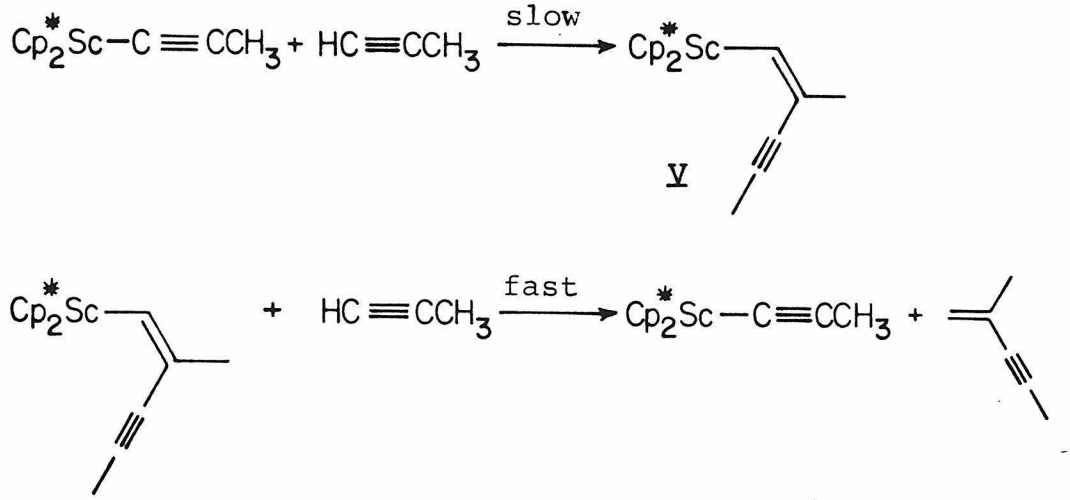
RESULTS AND DISCUSSION

Reactions of alkynes with $Cp^*_2ScCH_3$ and Cp^*_2ScH. As previously mentioned, Cp^*_2ScR (R = H, CH_3) react with propyne to give RH and $Cp^*_2ScC{\equiv}CCH_3$. This scandium propyde complex is a catalyst for the dimerization of propyne (eq 1).



(1)

Trimers or oligomers are not observed in the reaction. The likely mechanism for this reaction is shown in Scheme 1.

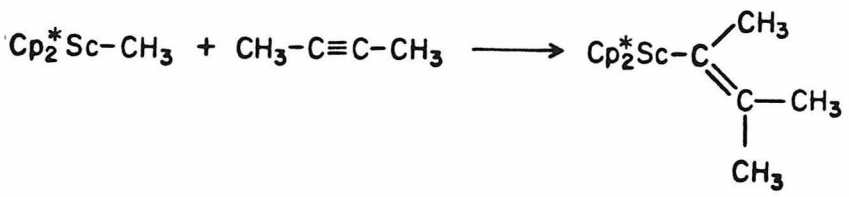


Scheme 1

In the slow step of this mechanism propyne inserts into the scandium-propyde bond, giving a vinyl complex (V). In a subsequent fast reaction, V reacts with the sp C-H bond of propyne to give 2-methyl-1-pentene-3-yne and regenerate

$Cp^*_2ScC{\equiv}CCH_3$. If the activation of an sp C-H bond is significantly faster than the alkyne insertion step, only dimers would be expected. Similar reactivity and mechanism were reported by Threlkel for several permethyltitanocene complexes.[10]

$Cp^*_2ScCH_3$ reacts stoichiometrically with 2-butyne, giving the alkyne inserted product (eq 2).



(2)

Prolonged reaction time and heating do not lead to any further insertions.

Ethylene polymerization by permethylscandocene alkyl and hydride complexes. At room temperature Cp^*_2ScR complexes (R = H, CH_3, $CH_2C_6H_5$) are active homogeneous catalysts for the polymerization of ethylene. These polymerization experiments were done with one atmosphere or less of ethylene over the catalyst solutions. Cp^*_2ScCl and $Cp^*_2ScC_6H_5$ do not react with ethylene under these conditions. When $Cp^*_2ScCH_3$ and $Cp^*_2ScCH_2C_6H_5$ were treated with 3 and 10 equivalents of ethylene, respectively, at -78°C and slowly warmed to room temperature, the ethylene was totally consumed by less than half of the scandium complex, suggesting that the chain initiation step (first insertion) is

slower than the chain propagation step (subsequent insertions). We feel that this is probably due to steric and electronic effects. The scandium-methyl bond is probably stronger than other scandium-alkyl bonds,[11] thus $Cp^*_2Sc-CH_3$ would have a higher barrier to insertion than $Cp^*_2Sc-CH_2CH_2CH_3$ or $Cp^*_2Sc-CH_2(CH_2)_nCH_3$, if Sc-C bond breaking is significant in the transition state. $Cp^*_2ScCH_2C_6H_5$ should have a more sterically congested coordination sphere than its first insertion product ($Cp^*_2ScCH_2CH_2CH_2C_6H_5$), making the benzyl complex less open to insertion of ethylene than $Cp^*_2ScCH_2CH_2CH_2C_6H_5$. Consequently, the products of ethylene insertion into $Cp^*_2Sc-CH_2C_6H_5$ would be expected to be better ethylene polymerization catalysts than the parent $Cp^*_2ScCH_2C_6H_5$ complex.

These polymerization experiments were generally run until the reaction stopped taking up ethylene. At this point the solution was cloudy, due to precipitated polyethylene. The excess ethylene was removed <u>in vacuo</u>, and HCl gas admitted into the reaction vessel to cleave the scandium-polymer bonds. The IR spectrum of this polymer (Figure 1) shows bands typical of polyethylene [12] as well as three bands at 1643, 990 and 910 cm^{-1}, which are characteristic of vinyl groups in polyethylene.[13] When the polymer is treated with Br_2(gas) the three bands disappear, which is consistent with their assignment as vibrations due to vinyl groups. From the relative intensities of the bands at 910 cm^{-1} (due to $RCH=CH_2$) and 1378 cm^{-1} (due to RCH_3) and their relative

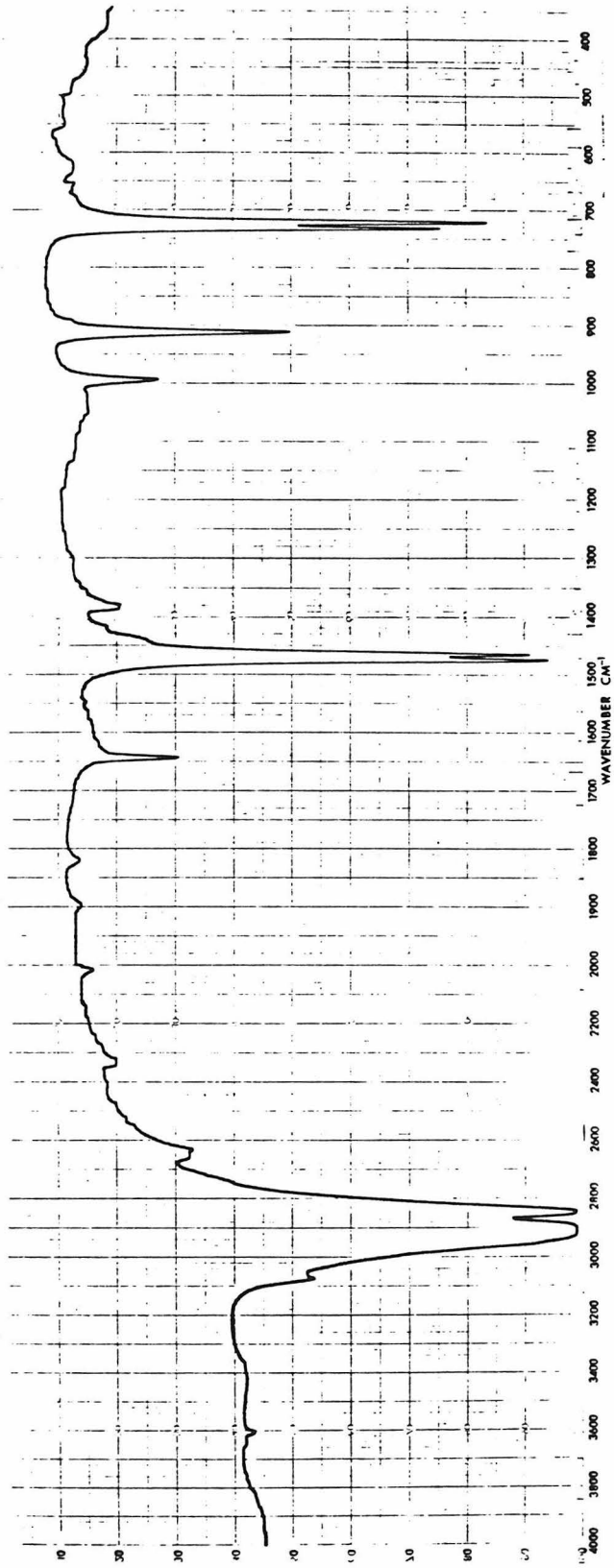


Figure. IR spectrum of polyethylene from the reaction of $Cp^*_2ScCH_3$ with $H_2C{=}CH_2$.

extinction coefficients [14] the ratio of methyl to vinyl groups was determined to be 1.7:1, respectively. The molecular weight of this polymer is 1700 ± 300 G/mole, and its polydispersity ($\overline{M}_w/\overline{M}_n$) is 1.7 ± 0.3. This polydispersity is very low,[15] which is generally found in catalyst systems where chain termination does not occur at an appreciable rate;[16] the polymer yields in these systems are one or less polymer chain per catalyst molecule. One mole of $Cp^*_2ScCH_3$ produces 1.7 ± 0.2 moles of polyethylene, indicating that chain termination must be occurring. A low polydispersity in a system with significant chain termination is difficult to reconcile. The low molecular weight of the polymer is most likely responsible for this anomaly. The polymer was washed several times with organic solvents during isolation. When these washings were evaporated to dryness a sticky polymer residue was left. In washing the polymer, lower molecular weight material was removed that would have made the polydispersity higher.

The presence of vinyl groups in the isolated polymer suggests β-hydrogen elimination may be an active chain termination pathway, which would lead to polyethylene with one methyl and one vinyl end group (eq 3).

$$Cp^*_2ScCH_2(CH_2)_nCH_3 \longrightarrow Cp^*_2ScH + H_2C{=}CH(CH_2)_{n-1}CH_3 \quad (3)$$

The polymer prepared from $Cp_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$ (Cp = $\eta\text{-}C_5H_5$) has a number average molecular weight of 160,000 to

190,000 and a weight average molecular weight of 740,000 to 2,340,000.[8] Thus the polydispersity for this polymer is ca. 9. The average molecular weight for this polyethylene is much larger than that found in our system, which may be a result of greater steric interactions for the Cp* system accelerating its rate of chain termination relative to $Cp_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$. The polydispersity of the two systems can not be directly compared, since the polydispersity of the polyethylene from $Cp^*_2ScCH_3$ is probably anomalously small.

If the catalyst/polymer solutions are treated with air, rather than HCl, to cleave the scandium-polymer bonds, a polymer with a carboxylic acid end group is formed (i.e. $HOOC(CH_2)_nCH_3$). This polymer gives an IR spectrum with the same bands as polyethylene formed by addition of HCl (Figure 1), as well as several additional large bands at 3400, 1560, 1400, 1090 and 500 cm^{-1}, the first four of which are characteristic of a carboxylic acid functionality.[17]

The melting points of the polyethylene formed by these scandium complexes range from 118 to 125°C, indicating that the polymer is highly crystalline.[18] The IR spectra show very narrow bands, which are also consistent with high crystallinity and a highly regular polymer chain.

Olefin and alkyne hydrogenation catalyzed by Cp^*_2ScH. In addition to being a catalyst for ethylene polymerization,

Cp^*_2ScH is a catalyst for the hydrogenation of olefins and alkynes at 25°C. Terminal and internal linear olefins, as well as isobutylene are hydrogenated by H_2 in the presence of Cp^*_2ScH. Internal alkynes are hydrogenated to their respective alkenes and alkanes. Trisubstituted olefins are not hydrogenated by Cp^*_2ScH. 2-methyl-2-butene does not react with Cp^*_2ScH/H_2 after thermolysis for long periods of time. When 2-methyl-2-butene was treated with Cp^*_2ScD/D_2, however, H/D exchange was observed at the vinylic position (eq 5).

$$Cp^*_2ScD + \underset{H}{\diagup\!=\!\diagdown} \longrightarrow Cp^*_2ScH + \underset{D}{\diagup\!=\!\diagdown} \qquad (5)$$

<u>Stoichiometric reactions of $Cp^*_2ScCH_3$ and Cp^*_2ScH with olefins.</u> $Cp^*_2ScCH_3$ reacts with propene in cyclohexane solvent to give $Cp^*_2ScCH{=}CHCH_3$-<u>t</u> and isobutane (eq 6).

$$Cp^*_2ScCH_3 \xrightarrow[25^oC]{H_2C{=}CHCH_3} Cp^*_2ScCH{=}CHCH_3\text{-}\underline{t} + HC(CH_3)_3 \qquad (6)$$

The trans configuration of the propenyl ligand was assigned based on the large coupling constant between the two vinylic protons ($^3J_{H-H}$ = 19 Hz). Isolation of $Cp^*_2ScCH{=}CHCH_3$-<u>t</u> has proven impossible. Although reaction 7 gives a 85-90% yield by ^1H NMR, removal of the solvent and attempted isolation of the product gives only an impure oil in low yield (10-15%). Treatment of Cp^*_2ScCl with $LiCH{=}CH(CH_3)$ leads to the same

impure oil. We are confident in our assignment of this complex as $Cp^*_2ScCH=CHCH_3$-*t*, however, because its NMR and IR spectra are very similar to those of analogous zirconium and hafnium complexes.[19]

In the presence of excess propene (10 equivalents), reaction 7 appears to go in two stages. $Cp^*_2ScCH_3$ is converted to a new compound before an appreciable amount of isobutane is released. This new compound has a single Cp* resonance ca. 0.03 ppm downfield of $Cp^*_2ScCH_3$, and two doublets at 0.78 and 0.41 ppm with coupling constants of 6 and 8 Hz, respectively. The downfield doublet is roughly three times larger than the upfield one. This spectrum is consistent with a scandium isobutyl complex, $Cp^*_2ScCH_2CH(CH_3)_2$, where the isobutyl methyl groups give rise to the downfield doublet and the methylene group of the isobutyl is responsible for the upfield doublet.[20] Isolation of this intermediate complex was not possible, since it decomposed on removal of propene and solvent. Attempts to prepare Cp^*_2Sc-*i*-butyl by alternate routes also met with failure. Treatment of Cp^*_2ScCl with $LiCH_2CH(CH_3)_2$ leads only to decomposition of the scandium complex, and treatment of Cp^*_2ScH with isobutylene leads only to a scandium isobutenyl complex (*vide infra*). In the second stage of the reaction, the isobutyl complex reacts with propene to give $Cp^*_2ScCH=CHCH_3$-*t* and isobutane. Propene insertion into the scandium-isobutyl bond does not occur, since the reaction of

the inserted product (Cp^*_2Sc-2,4-dimethylpentyl) with the C-H bond of propene would give 2,4-dimethylpentane, which is not observed by ^1H NMR or gas chromatography (G.C.). The proposed reaction path is shown in equation 8.

$$Cp^*_2ScCH_3 \xrightarrow[(a)]{H_2C=CHCH_3} [Cp^*_2ScCH_2CH(CH_3)_2] \qquad (8)$$

$$\downarrow (b)\ H_2C=CHCH_3$$

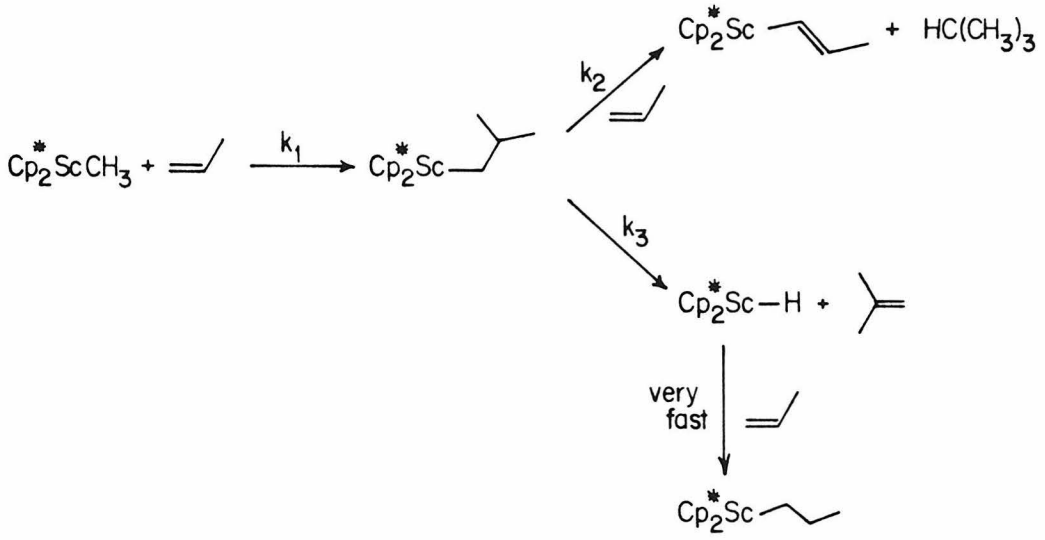
$$Cp^*_2ScCH=CHCH_3\text{-}\underline{t} + CH(CH_3)_3$$

Under these experimental conditions ([propene]/[$Cp^*_2ScCH_3$] = 10, 25°C) the half-life for the insertion reaction (eq 8(a)) is *ca.* one hour, while that of the C-H activation reaction (eq 8(b)) is *ca.* six hours. The scandium isobutyl complex probably reacts directly with a vinylic C-H bond. Reaction with an allylic C-H bond to give $Cp^*_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$, followed by isomerization of the allyl ligand to a propenyl ligand does not occur. When $Cp^*_2Sc(\eta^3\text{-}CH_2CH{=}CH_2)$ is pyrolyzed either alone or in the presence of excess propene at 80°C, no change is observed in the ^1H NMR spectrum of the allyl complex.

When $Cp^*_2ScCH_3$ is treated with only a stoichiometric amount of propene (2 equivalents), the reaction is not as simple as equation 7. Rather, isobutene and $Cp^*_2ScCH_2CH_2CH_3$ are observed in addition to the other products (eq 9).

$$Cp^*_2ScCH_3 + 2\ H_2C{=}CHCH_3 \longrightarrow Cp^*_2ScCH{=}CHCH_3\text{-}t + Cp^*_2ScCH_2CH_2CH_3 + H_2C{=}C(CH_3)_2 + CH(CH_3)_3 \quad (9)$$

A similar result is obtained when the reaction of $Cp^*_2ScCH_3$ with excess propene is carried out at elevated temperatures (80^oC). A mechanism that accounts for these observations is shown in Scheme 2.



Scheme 2

If k_2[propene] is large relative to k_3, β-hydride elimination will be a minor pathway. With high concentrations of propene, this may be the case. If the concentration of propene is reduced, however, k_3 may become comparable to k_2[propene] and β-hydride elimination would be observed.

The effect of temperature on the product distribution is also consistent with the proposed mechanism. A given increase in temperature generally increases the rate of a unimolecular reaction more than a bimolecular one, because of a more favorable entropy of activation for the unimolecular reaction. Thus raising the temperature of this reaction would make the β-hydride elimination reaction (unimolecular) competitive with the reaction to give $Cp^*_2ScCH{=}CHCH_3$-t (bimolecular), and isobutylene would observed.

Watson has examined the reaction of $Cp^*_2LuCH_3$ with propene.[7] Under reaction conditions similar to those used for reaction 8 ([propene]/[$Cp^*_2LuCH_3$] = 10, 22°C), rapid insertion of propene into the Lu-CH_3 bond is observed, forming Cp^*_2Lu-i-butyl. The rate of this insertion reaction is roughly 200 times faster than the analogous scandium insertion reaction (eq 8(a)).[21] Cp^*_2Lu-i-butyl then inserts a second molecule of propene to give Cp^*_2Lu-2,4-dimethylpentyl, or β-hydrogen eliminates to give isobutene and Cp^*_2LuH, which readily reacts with propene to give $Cp^*_2LuCH_2CH_2CH_3$. If the decomposition of Cp^*_2Lu-i-butyl is monitored in the absence of propene, several lutetium complexes are observed: consisting of Cp^*_2LuR, where R = CH_3, -η^3-$CH_2CH{=}CH_2$, -η^3-$CH_2C(CH_3){=}CH_2$, $CH{=}C(CH_3)_2$. β-methyl elimination is proposed to account for the formation of $Cp^*_2LuCH_3$, and labeling studies suggest the intermediacy of $Cp^*Lu(\eta^5\text{-}C_5(CH_3)_4CH_2$ in the formation of the al-

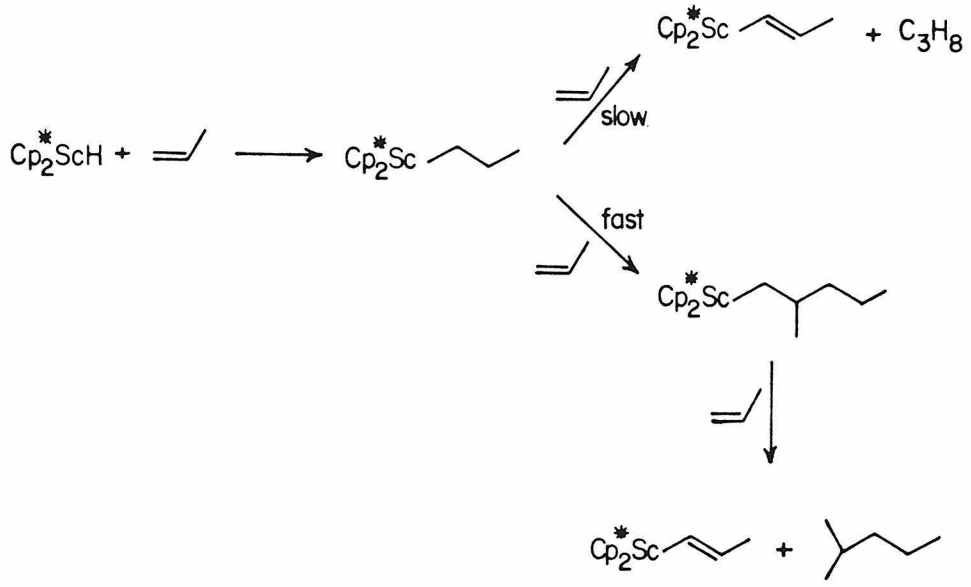
lylic and vinylic complexes.[22] In contrast, the reaction of Cp^*_2Sc-*i*-butyl with propene (eq 8(b)) probably involves direct vinylic C-H activation, since a deuterium isotope effect ($k_{propene}/k_{d_6\text{-propene}}$) of greater than five was observed.[23] If formation of $Cp^*Sc(\eta^5\text{-}C_5(CH_3)_4CH_2)$ were rate determining, an isotope effect would not be expected. And, if $Cp^*\overline{Sc(\eta^5\text{-}C_5(CH_3)_4CH_2)}$ were an intermediate in this reaction and its formation was not the rate determining step, then it should have been observed in the reactions of $Cp^*_2ScCH_3$ with either propene or *d*$_6$-propene.

Cp^*_2ScH reacts with propene to give $Cp^*_2ScCH{=}CHCH_3$-*t* (eq 11).

$$Cp^*_2ScH \xrightarrow{H_2C=CHCH_3} Cp^*_2ScCH{=}CHCH_3\text{-}t + C_3H_8 + C_6H_{14} \qquad (11)$$

$Cp^*_2ScCH_2CH_2CH_3$ is a likely intermediate in this reaction, since it is the only scandium species observed in the initial ^1H NMR spectrum. The scandium propyl complex has two modes of reactivity. First it reacts directly with propene to give propane and the scandium propenyl complex. In a second, more rapid reaction, a new compound is formed that has a Cp* resonance shifted slightly downfield of $Cp^*_2ScCH_2CH_2CH_3$ and a doublet at 0.64 ppm with a coupling constant of 6 Hz. The coupling constant and chemical shift of this doublet are very similar to those observed for the proposed Cp^*_2Sc-*i*-butyl isobutyl methyl groups. The most

likely candidate for this new compound is Cp^*_2Sc-2-methylpentyl , formed by insertion of propene into the scandium-propyl bond. This new compound slowly reacts with propene to give $Cp^*_2ScCH{=}CHCH_3$-$\underline{t}$ and 2-methylpentane (^1H NMR). A mechanism consistent with these observations is shown in Scheme 3.



Scheme 3

G. C. analysis of the volatiles from this reaction show 2-methylpentane and a small amount (<1%) of higher molecular weight alkanes were formed, indicating that insertion of propene into Cp^*_2Sc-2-methylpentyl is very slow relative to vinylic C-H activation.

Neither $Cp^*_2ScCH_2C_6H_5$ nor $Cp^*_2ScC_6H_5$ react with propene, except at high temperatures, where the products of their reactions decompose. Isolated $Cp^*\overline{Sc(\eta^5\text{-}C_5(CH_3)_4CH_2)}$ (dimeric or oligomeric, vide supra) reacts with propene to give a complex mixture of products, but no $Cp^*_2ScCH{=}CHCH_3$-t is formed.

Cp^*_2ScH reacts with trans-butene to give a single scandium species. The expected product was $Cp^*_2ScCH(CH_3)CH_2CH_3$, however, treatment of this complex with D_2O yields $CH_3CH_2CH_2CH_2D$, suggesting that the scandium species is actually $Cp^*_2ScCH_2CH_2CH_2CH_3$. This type of alkyl ligand rearrangement is common for early transition metal complexes.[24]

$Cp^*_2ScCH_3$ reacts cleanly with isobutylene to give methane and a scandium isobutenyl complex (eq 12).

$$Cp^*_2ScCH_3 + 2\ H_2C{=}C(CH_3)_2 \longrightarrow Cp^*_2ScCH{=}C(CH_3)_2 + CH_4 \qquad (12)$$

Neither a scandium neopentyl complex or neopentane are observed, indicating that isobutylene does not insert into the scandium-methyl bond. $Cp^*_2ScCH{=}C(CH_3)_2$ was isolated as a pure pale yellow solid. This reaction is analogous to the reaction of $Cp^*_2ScCH_3$ with styrenes (vide supra), but the rate of this reaction is roughly 50 times slower, possibly due to the greater steric bulk of isobutylene. Cp^*_2ScH re-

acts with isobutylene to give the scandium isobutenyl complex and isobutane (eq 12).[25]

$$Cp^*_2ScH + 2\ H_2C{=}C(CH_3)_2 \longrightarrow Cp^*_2ScCH{=}C(CH_3)_2 + HC(CH_3)_2 \quad (12)$$

The reactions of Cp^*_2ScR complexes (R = H, CH_3, $CH_2C_6H_5$) with olefins consist of insertion and C-H activation reactions. In virtually every mechanism for olefin insertion into transition metal-alkyl or -hydride bonds the olefin donates electron density form its π cloud into a vacant orbital on the metal center prior to insertion.[2, 26] We believe that this is the case for scandium as well, and the ability of the olefin's π cloud to approach the metal center is strongly dependent on the steric bulk of both the olefin and the ligand on scandium. Similar arguments have been made concerning olefin polymerization by Ziegler-Natta catalysts.[1(a)] Ethylene readily inserts into Cp^*_2Sc-H, Cp^*_2Sc-CH_3 and Cp^*_2Sc-$CH_2C_6H_5$ bonds, but is unreactive toward Cp^*_2Sc-C_6H_5 bonds. The phenyl ligand presumably blocks the active site from reacting with the ethylene π cloud. Unfavorable steric effects are probably responsible for propene not inserting into Cp^*_2Sc-i-butyl and Cp^*_2Sc-2-methylpentyl bonds, while it inserts readily into the less sterically demanding propyl ligand of Cp^*_2Sc-$CH_2CH_2CH_3$. A β-disubstituted alkyl ligand appears to be too bulky to allow interaction with propene's π cloud

(leading to insertion) in this system. In support of this, $Cp^*_2ScCH_2C_6H_5$ is unreactive toward propene. The steric bulk of the olefin controlling reactivity is seen in the reactions of $Cp^*_2ScCH_3$ with propene and isobutylene. Propene inserts into the $Cp^*_2Sc-CH_3$ bond, whereas isobutylene does not.

The observation of facile vinylic C-H bond activation by scandium alkyl complexes suggests an alternate chain termination pathway in the polymerization of ethylene by these complexes. Because of the significant number of vinyl end groups in the isolated polyethylene, we proposed β-hydride elimination was the primary chain termination pathway. Activation of a vinylic C-H bond of ethylene by the scandium-polymer complex, however, would also lead to chain termination. The catalyst product of this reaction would be a scandium vinyl complex (eq 12).

$$Cp^*_2ScCH_2(CH_2)_nCH_3 + H_2C{=}CH_2 \longrightarrow Cp^*_2ScCH{=}CH_2 + CH_3(CH_2)_nCH_3 \quad (12)$$

The newly formed vinyl complex could then act as a polymerization catalyst, giving a polymer with a vinyl end group. Ziegler-Natta catalysts are very electrophilic and may activate vinylic C-H bonds in a similar manner. Although this termination pathway is applicable to vinyl end groups, it can not form vinylidene end groups, which are often observed in oligomers formed by Ziegler-Natta catalysts. Successive

insertion and β-hydride elimination steps are generally used to explain vinylidene end groups.[27]

The differences in reactivity of Cp^*_2LuR versus Cp^*_2ScR (R = CH_3, -i-butyl) toward olefins are probably caused by steric effects. Lu has a 0.10 Å larger ionic radius than Sc, making lutetium's active site more open and thereby decreasing steric interactions. Similar steric effects were proposed to explain the rate difference for the reactions of $Cp^*_2ScCH_3$ and $Cp^*_2LuCH_3$ with methane (vide supra). Thus propene reacts 200 times faster with $Cp^*_2LuCH_3$ than with $Cp^*_2ScCH_3$, because the π cloud of the olefin can interact with the Lu atom of $Cp^*_2LuCH_3$ more readily than it can with the Sc atom of $Cp^*_2ScCH_3$. Unfavorable steric interactions probably prevent the insertion of propene into $Cp^*_2Sc\text{-}CH_2CRCH_3$ (R = methyl, propyl) bonds, while propene inserts readily into Cp^*_2Lu-i-butyl bonds.

The differing ionic radii of Sc and Lu may also be responsible for the apparent difference in the mechanisms of their C-H activation reactions. Cp^*_2Sc-i-butyl appears to react directly with the C-H bond being activated, while $Cp^*\overline{Lu(\eta^5\text{-}C_5(CH_3)_4CH_2)}$ is the postulated intermediate for the reaction of Cp^*_2Lu-i-butyl with C-H bonds.[22] The smaller ionic radius of Sc should shorten the M-CH_2 bond (M = Sc, Lu) of $Cp^*\overline{Sc(\eta^5\text{-}C_5(CH_3)_4CH_2)}$ relative to $Cp^*\overline{Lu(\eta^5\text{-}C_5(CH_3)_4CH_2)}$.[28] Shortening the M-$CH_2$ bond should

pull the methylene further below the plane of the Cp* ligand, giving $Cp^*Sc(\eta^5\text{-}C_5(CH_3)_4CH_2)$ greater strain energy than $Cp^*Lu(\eta^5\text{-}C_5(CH_3)_4CH_2)$. Thus, while the lowest energy pathway for C-H activation by Cp^*_2Lu-i-butyl is via $Cp^*Lu(\eta^5\text{-}C_5(CH_3)_4CH_2)$, the greater strain energy of $Cp^*Sc(\eta^5\text{-}C_5(CH_3)_4CH_2)$ may make this pathway higher in energy than direct C-H activation by Cp^*_2Sc-i-butyl.

EXPERIMENTAL

General Considerations. All manipulations were carried out using either high vacuum line or glove box techniques. All solvents were purified by distillation from Na or CaH_2, followed by vacuum transfer from titanocene. Isobutylene was dried with sodium and stored in a thick walled glass bomb over Na/benzophenone. All other gaseous reagents were freeze-pump-thawed twice and distilled from a -30°C trap just prior to use. All liquid reagents were dried over 4 Å molecular sieves, and freeze-pump-thawed twice before use. NMR solvents, d_6-benzene and d_{12}-cyclohexane, were vacuum transferred from activated 4 A molecular sieves, then from titanocene.

^1H NMR spectra were run on Varian EM-390 (C.W., 90 MHz) and JEOL FX-400Q (F.T., 400 MHz) spectrometers. ^2H NMR spectra were run on a JEOL FX-90Q (F.T., 13.8 MHz) spectrometer. All spectra of new compounds are listed in Table. Infrared (IR) spectra of polyethylene were run as KBr pellets and other samples were run as Nujol mulls on KBr plates. IR spectra were recorded on a Beckman IR-2420 spectrometer. Analyses were performed by the Caltech Analytical Laboratory.

Many of the reactions in this chapter were carried out in NMR tubes. Any experiment discussed in this chapter and not listed below was carried out in a sealed NMR tube with ca. 20 mg of the scandium complex in ca.

Table. ^{1}H and ^{13}C NMR spectroscopic data.*

Compound	Assignment	(ppm)	Coupling	Comments
$Cp^*_2ScC(CH_3)=C(CH_3)_2$	a	1.85 s		500 MHz
a b c + d	b + c + d	2.89 s 1.53 s 1.13 s		
$Cp^*_2ScCH=C(CH_3)_2$	a	1.90 s		
a b c	b	6.12 s		
	c	2.20 s		
	c	1.57 s		
$Cp^*_2ScCH=CHCH_3$-t	a	1.90 s		
a b c d	b	7.0 d q	J_{bc} = 19.5; J_{bd} = 1.5	
	c	5.25 d q	J_{cd} = 5.4	
	d	2.18 d d		

Compound	Assignment	(ppm)	Coupling	Comments
$Cp^*_2Zr(CH=CHCH_3\text{-}t)_2$	a	1.76 s		ref. 19
a b c d	b	5.83 d q	$J_{bc} = 18$; $J_{bd} = 1.5$	
	c	5.21 d q	$J_{cd} = 5.5$	
	d	1.90 d d		
$Cp^*_2Hf(CH=CHCH_3\text{-}t)_2$	a	1.79 s		ref. 19
a b c d	b	5.56 d q	$J_{bc} = 18$; $J_{bd} = 1.5$	
	c	5.24 d q	$J_{cd} = 5.5$	
	d	1.88 d d		
$Cp^*_2ScCH_2CH_2CH_2CH_3$	a	1.88 s		400 MHz
a b c d e	b	0.90 t	7.4	
	c + d + e	0.56-0.61		
	a	119.29, 11.42		$^{13}C\ \{^1H\}$ 400 MHz
	b	43.43		
	c	34.47		
	d	30.70		
	e	14.49		

* Unless otherwise specified, spectra were taken in C_6D_6 at ambient temperature at 90 Mhz. The chemical shifts are reported in relative to TMS or residual protons of the solvent. Coupling constants are reported in Hz.

Ø.35 mL of d_{12}-cyclohexane. The spectra were referenced to internal TMS or the protio impurity of the solvent ($C_6D_{11}H$). A measured amount of each of the appropriate reagents was added to the tube before it was cooled to +196°C and sealed with a torch.

The molecular weight and polydispersities reported in this chapter were measured, using gel permeation chromatography, by Dr. Howard Turner at Exxon Chemical Co., Baytown, Texas.

Preparation of $Cp^*_2ScC(CH_3)=C(CH_3)_2$. A solution of 218 mg. of $Cp^*_2ScCH_33$ (Ø.66 mmol) in 5 mL of petroleum ether was treated with ca. 2 mL of 2-butyne. The reaction mixture was stirred for 4Ø minutes at room temperature and the volatiles removed in vacuo. Fresh petroleum ether (2 mL) was added to the resulting solid and the clear solution cooled to -78°C. A pale yellow solid product precipitated and was collected by filtration (135 mg, 53%). IR data (cm^{-1}): 271Ø(w), 267Ø(w), 161Ø(m), 126Ø(w), 12ØØ(w), 116Ø(w), 115Ø(w), 1Ø9Ø(w), 1Ø6Ø(w), 1Ø2Ø(s), 8ØØ(w), 78Ø(w), 745(w), 72Ø(m), 66Ø(m). Anal. calc. for $C_{25}H_{39}Sc$: C, 78.Ø9; H, 1Ø.22. Found: C, 77.78; H, 1Ø.23.

Preparation of $Cp^*_2ScCH=C(CH_3)_2$. $Cp^*_2ScCH_3$ (275 mg., Ø.83 mmol) was dissolved in 5 mL of petroleum ether in a viscous walled glass bomb. Approximately one mL of isobutylene was then condensed into the bomb, and it was

heated to 80°C for 20 hours. After cooling the bomb to room temperature, the isobutylene was allowed to boil off. After concentrating the solution to 2 mL, it was cooled to -78°C. The white solid product precipitated and was isolated by filtration (230 mg, 75%). IR data (cm^{-1}): 2715(w), 2695(w), 1584(s), 1498(w), 1260(w), 1114(w), 1080(w), 1060(w), 1022(w), 790(s), 615(w), 589(w), 500(m), 447(m), 420(s). Anal. calc. for $C_{24}H_{37}Sc$: C, 77.80; H, 10.07. Found: C, 77.49; H, 10.01.

Dimerization of Propyne. A sealed NMR tube was prepared with 26 mg of $Cp^*_2ScCH_3$ (0.079 mmol), 0.4 mL of C_6D_6 and 0.55 mmol of propyne (7 equivalents). Within 30 minutes at room temperature, all of the propyne had been consumed; 2-methyl-1-pentene-3-yne, $Cp^*_2ScC\ CCH_3$ and methane were the only compounds observed in the NMR spectrum. The 2-methyl-1-pentene-3-yne was identified by comparison of its NMR to that of an authentic sample. [10] $Cp^*_2ScC\ CCH_3$ is most likely the catalyst for this dimerization because the reaction of $Cp^*_2ScCH_3$ is very fast at room temperature and treatment of $Cp^*_2ScCH_3$ with one equivalent of $HC\ CCH_3$ leads cleanly and quantitatively to $Cp^*_2ScC\ CCH_3$.

Polymerization of Ethylene. The procedure used for polymerization of ethylene by $Cp^*_2ScCH_3$ is described here, but $Cp^*_2Sc(THF)H$ or $Cp^*_2ScCH_2C_6H_5$ can be substituted for

$Cp^*_2ScCH_3$ and the same results are obtained. A solution of 35 mg of $Cp^*_2ScCH_3$ (Ø.11 mmol) in 1Ø mL of low boiling petroleum ether was treated with one atmosphere of ethylene in ca. 5ØØ mL. The pressure was maintained close to one atmosphere (Ø.1 atm) until ethylene uptake ceased (generally 2-3 hours). The excess ethylene was removed in vacuo and the cloudy to thick suspension was treated with 5Ø-1ØØ equivalents of HCl (gas). After 15 minutes the reaction vessel was opened to the air and the slurry filtered. The resulting polymer was washed several times with petroleum ether, once with acetone, once with water and finally with acetone. The polymer was dried in vacuo. The yield of polymer was Ø.3Ø g. Gel permeation chromatography measurements gave a molecular weight of 17ØØ ± 3ØØ g/mol and a polydispersity of 1.7 ± Ø.3. The yield of polymer chains per scandium atom was 1.7 ± Ø.2. The melting point of this polymer was 118-12Ø°C. IR data (cm^{-1}): 3Ø8Ø(w), 292Ø(s), 285Ø(s), 266Ø(w), 2638(w), 1644(m), 1485(s), 1464(s), 1378(w), 99Ø(m), 91Ø(m), 731(s), 72Ø(s). The IR spectrum is shown in Fig. 1 and the assignment of its bands is given in the text. The relative intensities of the IR bands of CH_3 groups (1378 cm^{-1}) and vinyl groups (91Ø cm^{-1}) are 1:4.3, respectively, from which we calculate a ratio of 1.7 methyl groups per vinyl group. [14] We were unable to obtain a ^{13}C NMR spectrum with an adequate signal to noise level to allow the calculation of the number of methyl or

vinyl groups per polymer chain (degree of branching). Both methyl and vinyl groups were observed, however, and their resonances were very small compared to the $(CH_2)_n$ signal, but accurate integration was not possible.

The Reaction of $Cp^*_2ScCH_3$ with Propene (Eq.(8)). A sealed NMR tube containing 20 mg of $Cp^*_2ScCH_3$ (0.06 mmol), 0.4 mL of C_6D_{12} and 0.64 mmol of propene was prepared. The reaction was monitored by ^1H NMR (90 MHz). The reaction is described in the text and the NMR spectra of $Cp^*_2ScCH_2CH(CH_3)_2$ and $Cp^*_2ScCH=CHCH_3$-t are listed in Table 1. The attempted synthesis of $Cp^*_2ScCH=CHCH_3$-t (similar work up to $Cp^*_2ScCH=C(CH_3)_2$) at 25°C and 80°C both yield only an impure oil (80-90% product). The IR spectrum of the oil was measured (cm^{-1}): 2660(w), 1565(m), 1530(w), 1250(w), 1150(w), 1020(s), 985(s), 795(w), 680(m), 660(s), 435(vs). The NMR spectrum of $Cp^*_2ScCH=CHCH_3$-t is very similar to those reported for the analogous zirconium and hafnium complexes $Cp^*_2M(CH=CHCH_3$-t$)_2$ (M=Zr, H). The NMR spectra of the zirconium and hafnium complexes are listed along with $Cp^*_2ScCH=CHCH_3$-t in Table 1, for comparison.

The Reaction of Cp^*_2ScH with Propene (Eq. (11)). A sealable NMR tube was charged with 20 mg of $Cp^*_2ScCH_3$ (0.06 mmol) and 0.4 mL of C_6D_{12}. The 14/20 joint connecting the NMR tube to the stopcock assembly was then

secured with several rubber bands. The tube was cooled to -196°C and one atmosphere of H_2 admitted to the tube. The stopcock was closed and the tube was warmed to room temperature. The NMR tube assembly was removed from the vacuum line and the solution agitated for five minutes, after which the solution was cooled to -196°C. The H_2 was evacuated and replaced with 0.72 mmol of propene. The tube was then sealed with a torch and warmed to room temperature. The initial NMR spectrum showed $CP^*_2ScCH_2CH_2CH_3$ as the only scandium species. The intermediates and products of the reaction are described in the text. The volatiles from this reaction were collected by breaking the NMR tube under vacuum and vacuum transferring the contents of the tube to a flask. Heat was applied to the apparatus holding the NMR tube and the vacuum transfer carried out for ca. one hour to ensure all the volatiles would transfer.

The Reaction of Cp^*_2ScH with Trans-Butene. A 40-mL thick walled glass bomb was charged with 330 mg of $Cp^*_2ScCH_3$ (1.0 mmol) and 10 mL of methylcyclohexane. The entire bomb was cooled to -196°C and one atmosphere of H_2 admitted. The bomb was warmed to room temperature and the solution stirred for 10 minutes. The bomb was cooled to -78°C and the H_2/CH_4 removed in vacuo. Trans-Butene (1.08 mmol) was admitted to the bomb at -78°C and the bomb allowed to come to room temperature. The

methylcyclohexane was removed and replaced with 2 mL of petroleum ether. Cooling this solution to -78°C precipitated a bright yellow solid (115 mg, 30%). We were unable to get a C,H analysis of this complex, presumably due to its thermal instability. When 14 mg of this complex (0.036 mmol) was treated with 8 μL of D_2O, only $CH_3CH_2CH_2CH_2D$ was observed, suggesting that the complex is $Cp^*_2ScCH_2CH_2CH_2CH_3$. The 400 MHz NMR spectrum of $CP^*_2ScCH_2CH_2CH_2CH_3$ (C_6D_{12}) shows a single Cp* resonance at 1.88 ppm, a triplet at 0.90 ppm with a coupling constant of 7.4 Hz and a broad multiplet 0.56-0.61 ppm. We assign the triplet to the α-CH_2 group and the broad multiplet to the remaining protons of the butyl ligand. A similar spectrum was obtained for $Cp^*_2ScCH_2CH_2CH_3$. A ^{13}C spectrum is observed that is consistent with $Cp^*_2ScCH_2CH_2CH_2CH_3$.

The Reaction of Cp^*_2ScH with Isobutylene (Eq. (12)).

A C_6D_{12} solution of Cp^*_2ScH was prepared as previously described and 1.2 equivalents of isobutylene added to it. After 30 minutes at room temperature, Cp^*_2ScH and $Cp^*_2ScCH=C(CH_3)_2$ were in equal concentration (^1H NMR). $Cp^*_2ScCH_2CH(CH_3)_2$ is not observed and the concentration of isobutane parallels the concentration of $Cp^*_2ScCH=C(CH_3)_2$. At the end of the reaction only $Cp^*_2ScCH=C(CH_3)_2$ and isobutane are observed. One explanation for these results involves C-H activation by Cp^*_2ScH, rather than by $Cp^*_2ScCH_2CH(CH_3)_2$. [25]

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21. The half-life for formation of Cp^*_2Lu-*i*-butyl is 0.2 hours for [propene]/[$Cp^*_2LuCH_3$] = 1, reference 21.

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23. $Cp^*_2ScCH_3$ reacts readily with d_6-propene to give $Cp^*_2ScCH_2CH(CH_3)(CD_3)$, at the same rate as normal propene. The next reaction (C-D activation as in eq 8(b)) is very slow, and β-deuteride elimination competes, so only an approximate rate of $Cp^*_2ScCD{=}CDCD_3$-*t* formation can be determined. β-deuteride elimination appears to be slower than β-hydride elimination from the scandium isobutyl complex, but we have been unable to quantify this.

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$$Cp^*_2ScH + H_2C{=}C(CH_3)_2 \rightleftharpoons Cp^*_2ScCH_2CH(CH_3)_2 \quad (13)$$

$$Cp^*_2ScH + H_2C{=}C(CH_3)_2 \overset{\text{fast}}{\rightleftharpoons} Cp^*_2ScCH{=}C(CH_3)_2 + H_2 \quad (14)$$

$$Cp^*_2ScCH_2CH(CH_3)_2 + H_2 \overset{\text{fast}}{\longrightarrow} Cp^*_2ScH + HC(CH_3)_2 \quad (15)$$

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28. The crystal structure of $Cp^*_2Lu(C,N\text{-}\eta^2\text{-}C_5H_4N)$ has been determined. The pyridyl ligand is disordered in a manner similar to that observed for $Cp^*_2Sc(C,N\text{-}\eta^2\text{-}C_5H_4N)$ (vide supra), such that the metal bound carbon and nitrogen are indistinguishable. The two averaged Sc-C and Sc-N bond lengths are 2.162(7) and 2.183(8) Å, while those of the isostructural lutetium complex are 2.274(6) and 2.270(6) Å. The difference in Sc versus Lu bond lengths almost exactly match their difference in ionic radii (0.10 Å).